the carbonyl stretching frequency of simple ketones to shorter wave lengths.[30] The carbonyl band of ethyl diazoacetate also exhibits a similar type of shift to that found in the case of the diazoketones. The bands of IX at 5.75, 5.83, 5.99 µ may be assigned to the carbonyl stretching of the acetoxy, carbethoxy and ketonic groups, respectively; the two higher bands are shifted to longer wave lengths than those associated with simple carbethoxy and ketonic groups, but the shift is smaller than in the case of the monocarbonyl diazo compounds, attributable to the cross conjugation of the diazo group with two carbonyl groups.

The very intense bands in the 7.2–7.5 µ region observed for all the diazoketones and diazoesters are useful for diagnostic purposes, but at present no firm basis exists for the proposal of a vibrational assignment. It may be significant that the azides also show an intense band in this region which has been assigned to the symmetrical stretching mode of the N–N–N group. However, in the case of diazohydrocarbons there are no strong bands in this region, and in the case of diazomethane, Crawford, Fletcher and Ramsay have assigned to the C–N stretching vibration a band at 11.7 µ.[12]

Finally, it may be noted that this and other recent investigations permit useful distinctions to be made between the positions of bands falling in the 4.4–5.3 µ region for several different types of compound (see Table III).

CAMBRIDGE, MASS.

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(30) Reference 19, p. 485; reference 23, p. 128.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

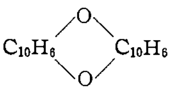
The Thermal Decomposition of Diazoöxides[1]

BY PETER YATES AND ERNEST W. ROBB[2]

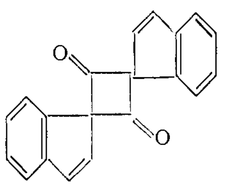
RECEIVED MAY 22, 1957

The product obtained by the decomposition of either naphthalene-1,2- or 2,1-diazoöxide in boiling xylene has been shown to be a 2-indenylidenenaphtho[1,2]-1,3-dioxole (XIII). It has been found to be accompanied by small amounts of its stereoisomer XIIIa. Thermal decomposition of naphthalene-2,1-diazoöxide in the presence of diphenylketene has been shown to give 2-benzohydrylidenenaphtho[1,2]-1,3-dioxole (XX). The mechanisms of these reactions are discussed.

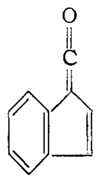
Although the course of the photolytic decomposition of diazoöxides has been elucidated in recent years as a result of the extensive work of Süs[3] and de Jonge[4] and their collaborators scant attention has been paid to the pyrolysis of this type of compound. Vaughan and Phillips[5] have observed that the gaseous products from the solid state pyrolysis of a number of diazoöxides consist mainly of nitrogen and carbon dioxide, while de Jonge[6] found that the same products are obtained when *o*-hydroxybenzenediazonium salts are heated in boiling water for some time. De Jonge proposed that the course of the thermal and photolytic decompositions are the same and that the carbon dioxide arises from decarboxylation of cyclopentadienecarboxylic acid derivatives, which have been shown to be formed in the course of the photolytic decomposition reactions.[3,4] However, neither he nor Vaughan[5] made any study of the non-gaseous products from the pyrolytic reactions. The only compounds which appear to have been examined in any detail are the naphthalene-1,2- and 2,1-diazoöxides. Bamberger[7] discovered that on heating either of these compounds in boiling xylene a product, $C_{20}H_{12}O_2$, m.p. 256°, was obtained which he formulated as a "bis-naphthalene-oxide" (I). Subsequently, Horner, Spietschka and Gross[8] investigated this product more thoroughly and came to the conclusion that the compound was the 1,3-cyclobutanedione derivative II formed by dimerization of the ketene III.



I



II



III

On the basis of the reported evidence the structure assigned seemed plausible; however, certain features of the degradative work appeared to us to require further clarification, *viz.* (i) the fact that the product obtained by hydrolysis of the pyrolysis product with aqueous acetic acid, which was assigned the formula $C_{20}H_{14}O_3$ and the structure IV, was not reported to undergo ready decarboxylation, although this would be anticipated on the basis of its formulation as both a β-keto acid and a cyclopentadienecarboxylic acid, (ii) the formation of a blue solution when this product was dissolved in aqueous sodium hydroxide, (iii) the observation that the compound obtained by hydrogenation of the hydrolysis product, which was assigned the formula $C_{20}H_{18}O_3$ and the structure V, gave a positive ferric chloride test, in spite of the fact that enolization of the ketone toward the carboxylic acid group of V is impossible. It was therefore de-

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(1) From the Ph.D. Thesis of Ernest W. Robb, Harvard University, 1956; a preliminary account of part of this work has appeared previously: P. Yates and E. W. Robb, *Chemistry & Industry*, 794 (1956).

(2) Public Health Service Research Fellow of the National Heart Institute, 1955–1956.

(3) O. Süs, *Ann.*, **556**, 65, 85 (1944); **579**, 133 (1953); O. Süs, M. Glos, K. Möller and H. D. Eberhardt, *ibid.*, **583**, 150 (1953); O. Süs and K. Möller, *ibid.*, **593**, 91 (1955); O. Süs, K. Möller and H. Heiss, *ibid.*, **598**, 123 (1956); O. Süs and K. Möller, *ibid.*, **599**, 233 (1956).

(4) J. de Jonge and R. Dijkstra, *Rec. trav. chim.*, **67**, 328 (1948); J. de Jonge, and R. Dijkstra, *ibid.*, **68**, 426 (1949); J. de Jonge, R. J H. Alink and R. Dijkstra, *ibid.*, **69**, 1448 (1950).

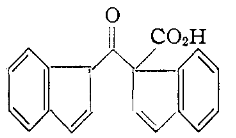
(5) J. Vaughan and L. Phillips, *J. Chem. Soc.*, 1560 (1947).

(6) J. de Jonge, R. Dijkstra and P. B. Braun, *Rec. trav. chim.*, **68**, 430 (1949).

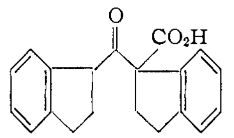
(7) E. Bamberger, M. Baum and L. Schlein, *J. prakt. Chem.*, **105**, 266 (1922).

(8) L. Horner, E. Spietschka and A. Gross, *Ann.*, **573**, 17 (1951).

cided to subject the structure of the pyrolysis product to further scrutiny.



IV

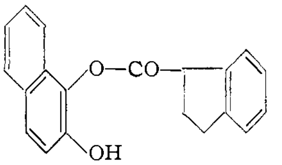


V

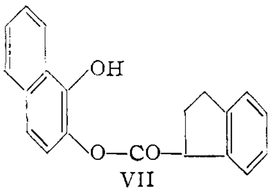
Naphthalene-2,1-diazoöxide was pyrolyzed by Bamberger's procedure[7] and gave, after chromatographic treatment of the crude product, a 36% yield of a lemon-yellow crystalline product which corresponded in melting point (256–257°), analysis and other properties to the product isolated by previous workers[7,8]; other fractions from the chromatographic separation yielded smaller amounts of highly colored materials which have not yet been investigated in detail. Examination of the infrared spectrum of the product, m.p. 256–257° (in $CHCl_3$) revealed a strong band at 5.91 μ accompanied by a weak band at 6.06 μ. This observation made it apparent that structure II was untenable for the pyrolysis product, since this should have a similar infrared spectrum in the double bond region to that of 1,1,3,3-tetramethyl-2,4-cyclobutanedione, which has two strong bands at 5.70 and 5.80 μ.[9] Confirmation of this view was obtained when the ultraviolet spectrum of the pyrolysis product was examined. A compound of structure II would be expected to show high intensity absorption only in the 250 mμ region, corresponding to the approximate summation of the absorption due to two indene residues[10,11]; however, its spectrum (in EtOH) was quite otherwise, with maxima at 214 mμ (log *e* 4.71), 278 mμ (log *e* 4.10) and 354 mμ (log *e* 4.32). Infrared and ultraviolet spectral comparisons confirmed the earlier reports[7,8] that the pyrolysis of naphthalene-1,2-diazoöxide gives a product (in 32% yield) identical with that obtained from the 2,1-diazoöxide.

Repetition of the hydrolysis of the pyrolysis product with aqueous acetic acid gave a white product, $C_{20}H_{14}O_3$, m.p. 187–189°, which, like the earlier reported product,[8] gave a positive ferric chloride test and dissolved in dilute aqueous sodium hydroxide to give a blue solution, but which, in contradistinction to the earlier observations, was found to be *insoluble* in aqueous sodium bicarbonate. Its infrared spectrum (KI disc) showed sharp bands at 2.95 μ(m) and 5.86 μ(s) and lacked the broad, intense band in the 3–4 μ region which is characteristic of carboxylic acids. These properties of the hydrolysis product are in much closer accord with the presence of a phenolic rather than a carboxylic acid group. The ultraviolet spectrum (in EtOH) of this product was complex, with maxima at 228 mμ (log ε 4.87), 277 mμ (log ε 3.92), 288 mμ (log ε 3.85), 323 mμ (log ε 3.48) and 331 mμ (log ε 3.45), but the position and very high intensity of the low wave length band gave the first indication that the compound might contain a naphthalene nucleus.

Hydrogenation of the hydrolysis product over palladium on charcoal led to the uptake of 1.02 molar equivalents of hydrogen and the formation of a *dihydro* compound, $C_{20}H_{16}O_3$, m.p. 125–127°.[12] This product, like its precursor, appeared to be a phenol rather than a carboxylic acid, since it was insoluble in aqueous sodium bicarbonate, soluble in aqueous sodium hydroxide to give a yellow solution, and gave a positive ferric chloride test; its infrared spectrum in the 2–4 μ region was also in accord with this view. The ultraviolet spectrum of the dihydro compound again indicated the presence of a naphthalene nucleus and was strikingly similar to that of β-naphthol (see Table I). The presence of a strong band in the infrared spectrum (in $CHCl_3$) at 5.69 μ was indicative of the presence of a lactone or a phenolic ester grouping.[13] The compound therefore was subjected to mild basic hydrolysis with aqueous sodium carbonate: 1-indanecarboxylic acid and 1,2-naphthalenediol were obtained in yields of 91 and 61%, respectively. The isolation of these products permits only two structures for the reduced hydrolysis product, VI or VII.



VI



VII

Esterified hydroxyl groups attached to the naphthalene nucleus, unlike free or etherified hydroxyl groups, have little effect on the ultraviolet spectrum[14]; hence, the spectra of VI and VII should resemble those of β- and α-naphthol, respectively.[15] The spectra of α-hydroxy- and α-methoxynaphthalene are sufficiently different from those of their β-isomers to permit distinction to be made readily; thus the α-substituted compounds have two groups of maxima centering at about 220 and 295 mμ while the β-substituted compounds show three groups of bands at about 225, 275 and 320 mμ.[14,17] The close similarity of the ultraviolet spectrum of the reduced hydrolysis product to that of β-naphthol already has been commented upon and may now be considered as decisively pointing to the structure VI for that product. It may further be

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[9] P. Fuchs, Ph.D. Thesis, Harvard, 1956.

[10] T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947).

[11] No high intensity absorption due to the presence of the 1,3-cyclobutanedione system is to be anticipated since Fuchs[9] has observed that although 1,1,3,3-tetramethyl-2,4-cyclobutanedione shows several bands in the 280–345 mμ region of the spectrum, none of these has a molecular extinction coefficient greater than 40; *cf.*, G. C. Lardy, *J. chim. phys.*, **21**, 353 (1924).

[12] When Raney nickel was used as the catalyst, a total of 2.12 molar equivalents of hydrogen was absorbed; the crude product had m.p. 102–106° (*cf.*, the m.p. of 110° reported for a supposed *tetrahydro* compound[8]), but on purification yielded material of m.p. 125–127°, identical with that obtained by the use of palladium on charcoal as a catalyst.

[13] R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," W. West, ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 455, 483.

[14] C. Daglish, THIS JOURNAL, **72**, 4859 (1950).

[15] It may be anticipated that the relatively low intensity contribution[16] from the isolated phenyl ring of the indane system will in no way vitiate this comparison.

[16] J. Entel, C. H. Ruof and H. C. Howard, *Anal. Chem.*, **25**, 1303 (1953).

[17] J. Jacques, M. Legrand and J. Bourdon, *Bull. soc. chim. France*, [5] **21**, 362 (1954); P. Ramart-Lucas, *ibid.*, [5] **17**, 259 (1950).

noted that the ultraviolet spectrum of the methyl ether, VIII, formed by the action of diazomethane on this compound, is also undoubtedly that of a β-naphthol ether (Table I).

TABLE I

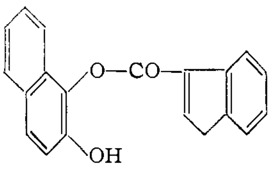
ULTRAVIOLET ABSORPTION SPECTRA OF VI AND VIII AND RELATED COMPOUNDS

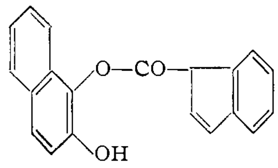
Compound	Solvent[a]	λmax, mμ (log ε) A[b]	B[b]	C[b]
VI	E	228(4.57)	266(3.71) 274(3.72) 283(3.66)	328(3.22)
VI	C	227(4.72)	266(3.72) 274(3.76) 288(3.68)	308(3.32) 315(3.26) 322(3.34) 329(3.10)[c]
β-Naphthol[d]	E	226(4.86)	265(3.59) 274(3.67) 285(3.52)	320(3.24) 330(3.31)
VIII	C	225(4.69)	267(3.54)[c] 273(3.60) 280(3.57)	306(2.88) 314(2.84) 321(2.94) 335(2.62)
β-Methoxynaphthalene[e]	E	227(4.85)	262(3.60) 272(3.65) 282(3.48)	314(3.18) 328(3.30)
		D[b]	E[b]	
α-Naphthol[d]	E	210(4.51)[f] 233(4.52)	285(3.65)[c] 296(3.71)	308(3.60)[c] 323(3.43)
α-Methoxynaphthalene	E	216(4.58) 231(4.52)	282(3.76) 293(3.81)	306(3.47) 320(3.36)

[a] E = ethanol; C = cyclohexane. [b] The absorption maxima are grouped in terms of the various band systems, *A–E*, into which they fall. [c] Inflection. [d] Reference 14. [e] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, *Anal. Chem.*, **23**, 1740 (1951). [f] This is an additional peak observed in the present work.

The previous report[8] that methylation of the "tetrahydro" compound[11] derived from the hydrolysis product, followed by hydrazinolysis, yielded *two* molar equivalents of 1-indanecarboxhydrazide seemed clearly incompatible with the present structural deductions. However, when VIII, the product obtained by methylation of VI, was treated with hydrazine, 1-indanecarboxhydrazide was obtained in 60% yield, based on the formation of *one* molar equivalent. A second, phenolic product, m.p. 73–75°, was also isolated from the reaction mixture and was converted to a benzoyl derivative, m.p. 108°, which is formulated as 2-methoxy-1-naphthyl benzoate (reported m.p. 110°).[18]

Mild basic hydrolysis of the acid hydrolysis product itself was also instructive; in this case 3-indenecarboxylic acid was isolated.[19] This established that the only structural change occurring on hydrogenation was the saturation of a double bond. Two structures are therefore possible for the acid hydrolysis product, IX and X. Of these the former may be chosen on the basis of the shift of the ester carbonyl band in the infrared spectrum to lower wave length on hydrogenation, which is explicable in terms of the presence of the conjugated ester function in IX.[20] Again the ultraviolet spectrum of the acid hydrolysis product and its methyl ether, prepared by reaction with diazomethane, were clearly related to β- rather than α-naphthol, although the relationship was not so clear-cut as in the case of VI because of the superimposition of absorption due to the 1-indenecarboxylate moiety. Two further observations require additional comment in terms of the newly proposed structures: (i) the report that both the acid hydrolysis product and its reduction product undergo diazo coupling[8]: it is suggested that, under the basic conditions normally used for coupling, VI and IX are hydrolyzed and it is the 1,2-naphthalenediol thus formed which undergoes the coupling; (ii) the blue coloration produced on dissolution of IX in aqueous base[8]; it has now been found that IX dissolves in degassed sodium hydroxide solution under nitrogen or in a basic solution containing sodium hydrosulfite *without* the formation of a blue color and it is therefore probable that the blue coloration is dependent on the formation of β-naphthoquinone by hydrolysis and air oxidation, since similar color reactions have been observed on mixing quinones with compounds containing a cyclopentadiene system in basic solution,[21] a fact which we have confirmed in the case of β-naphthoquinone.


IX


X

Hydrogenation of the pyrolysis product itself over palladium on charcoal led to the uptake of 1.01 molar equivalents of hydrogen and gave a lemon-yellow *dihydro* product, $C_{20}H_{14}O_2$, m.p. 199–201°. When Raney nickel was used as catalyst a total of 1.87 molar equivalents of hydrogen was absorbed, with a marked decrease in the rate of absorption after one molar equivalent had been absorbed; the product isolated, which had formerly been assumed to be a tetrahydro compound,[8,22] was identical with the *dihydro* compound above. This product had no bands in the hydroxyl region of its infrared spectrum (in CCl_4) and displayed a single sharp band in the double bond region at 5.80 μ. It was hydrolyzed readily by aqueous acetic acid to give a product identical with VI. The various hydro-

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(18) S. N. Chakravarti and V. Pasupati, *J. Chem. Soc.*, 1859 (1937).

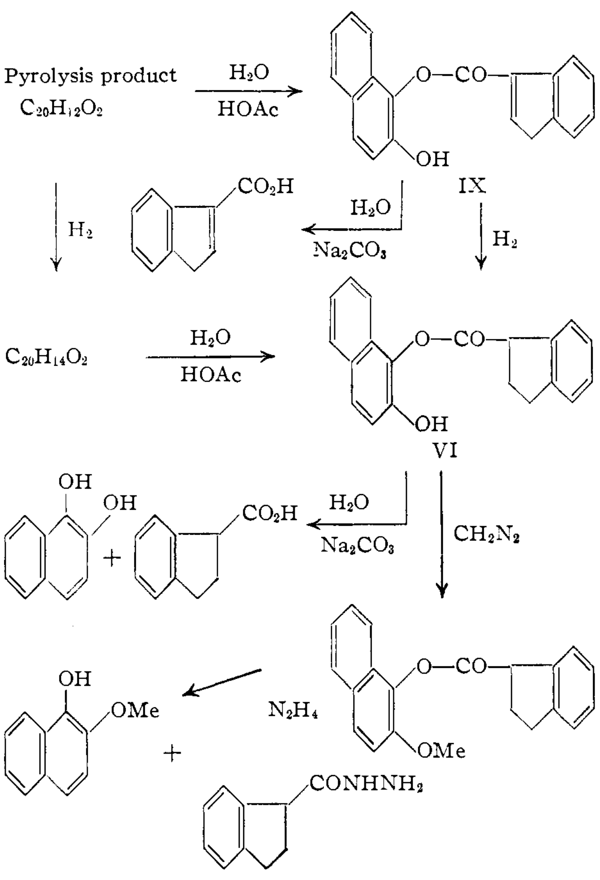
(19) This was identical with the product obtained by carboxylation of the sodium derivative of indene: *cf.*, W. S. Knowles, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.*, **7**, 374 (1942). This compound was previously considered to be 1-indenecarboxylic acid; however, the position of the carbonyl band in its infrared spectrum ($CHCl_3$ solution) at 5.90 μ bespeaks the presence of a *conjugated* carboxylic acid group (*cf.*, N. K. Freeman, THIS JOURNAL, **75**, 1859 (1952)) and we therefore designate it as the 3-carboxylic acid.

(20) This shift from 5.86 to 5.69 μ is anomalously large; however, the spectrum of IX was recorded in a KI disc while that of VI was taken in chloroform solution. It is probable that the unusually high wave length observed for IX, and hence the unusually large shift, is due to the fact that the spectrum was taken in the solid state, which could favor intramolecular hydrogen bonding (*cf.* ref. 12, p. 472); the difference between the spectra of IX and VI in the hydroxyl region is also in accord with this view. The complications due to change of medium were avoided by comparing the spectra of the methyl ethers of IX and VI in chloroform solution; in this case the shift from 5.75 to 5.68 μ was fully in harmony with the assigned structures.

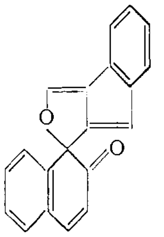
(21) W. Kesting, *Ber.*, **62**, 1422 (1929); A. P. Terent'ev and M. I. Ivanova, *J. Gen. Chem. U. S. S. R.*, **7**, 2087 (1937).

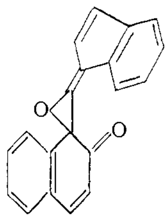
(22) It may be noted that the earlier analytical data[8] did not distinguish between the dihydro and tetrahydro formulations.

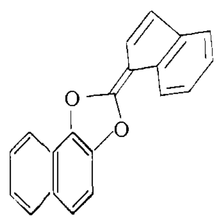
lytic and reductive transformations carried out on the pyrolysis product are summarized in the scheme



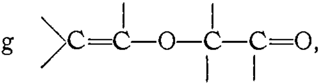
In a formal sense the pyrolysis product corresponds to a dehydration product of the phenol IX. Three structures, XI, XII and XIII, for the pyrolysis product appeared worthy of examination; each appeared capable of giving rise to IX by hydrolytic cleavage, although the route from XI would have to be tortuous.


XI


XII


XIII

Although no closely related model systems were available, it seemed probable that all of these systems would give rise to strong absorption in the ultraviolet in the near-visible region because of the presence in each of them of a ramified benzfulvene type system, *inter alia*. Initially, preference was given to structures XI and XII because of the presence of the intense bands at 5.91 and 5.80 μ in the infrared spectra of the pyrolysis product and its dihydro derivative, respectively; the position of these bands seemed not unreasonable for the carbonyl groups in either XI or XII and in the corresponding dihydro products with the double bond in conjugation with the ketone reduced.[23] However, there were grave obstacles to the acceptance of either structure XI or XII: (i) the formation of the *same* product on pyrolysis of either naphthalene-1, 2- or 2,1-diazoöxide was difficult to accommodate on this basis, (ii) the formulation for the dihydro compound made necessary by the infrared spectral considerations (*vide supra*) did not appear in accord with the observed fact that this compound is converted to VI on hydrolysis, (iii) treatment of the pyrolysis product with zinc failed to effect any change, although it would have been anticipated that a compound of structure XI or XII, which contains the grouping


$>C{=}\overset{|}{C}{-}O{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{C}{=}O,$

would readily undergo reductive cleavage of the C–O bond.

Structure XIII does not suffer from the disadvantages outlined above, but lacks a carbonyl group; further, the corresponding dihydro compound, which must be formulated as XIV in order to explain the hydrogenation and hydrolysis results, also lacks a carbonyl group. At first sight this seemed difficult to reconcile with the presence of the intense bands at 5.91 and 5.80 μ, respectively, in the infrared spectra of these compounds. However, McElvain and co-workers[24] have reported that simple ketene acetals, $R_1R_2C{=}C(OMe)_2$, have a major infrared band between 5.84 and 6.12 μ. A considerable increase in the intensity and shift to lower wave lengths of the ethylenic stretching bands of alkenes on substitution by fluorine or fluoroalkyl groups also has been reported.[25] Thus it appears that substitution by electronegative groups on a double bond, especially in unsymmetrical fashion, may lead to both an intensification and a shift to lower wave lengths of the ethylenic stretching band. Such a circumstance may be postulated for the inter-annular double bond in both XIII and XIV, allowing the possibility of the rationalization of the observed infrared spectra in terms of these structures.

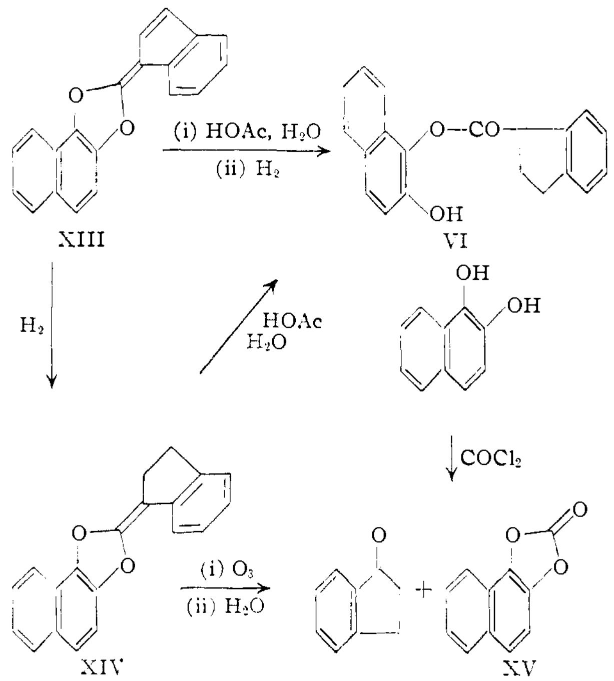
In order to establish the structure of the pyrolysis product on a firm degradative basis, the dihydro product was subjected to ozonolysis. Under mild conditions it was possible to isolate two major fragments by crystallization and chromatography. One of these was 1-indanone, identified as its semicarbazone and 2,4-dinitrophenylhydrazone. The other was the cyclic carbonate of 1,2-naphthalenediol, XV, which was identified by direct comparison with a sample synthesized from 1,2-naphthalenediol and phosgene. A small amount of phthalic acid also was isolated from the crude ozonolysis product; this undoubtedly arises from further degradation of

[23] Thus, we have found the carbonyl band in the case of 1-hydroxy-1-methyl-2(1*H*)-naphthalenone to be at 5.95 μ.

[24] S. M. McElvain and R. E. Starn, THIS JOURNAL, **77**, 4571 (1955); S. M. McElvain and G. R. McKay, *ibid.*, **77**, 5601 (1955).

[25] P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945); R. N. Haszeldine, *Nature*, **168**, 1028 (1951). It must be added that in the case of substitution by other halogens a shift in the opposite sense occurs (*cf.*, P. Yates, M. I. Ardao and L. F. Fieser, THIS JOURNAL, **78**, 650 (1956)); this may well be due to the intervention of *d*-orbital overlap, which is not possible for the first-row elements, fluorine and oxygen.

one or both of the major fragments. These results are summarized in the scheme



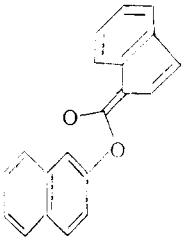
The discussion thus far has involved a tacit assumption with regard to the stereochemistry of XIII. In fact, two geometrical isomers of this type of structure are possible, the second being represented by XIIIa. It was therefore of interest to find that a *second product*, $C_{20}H_{12}O_2$, m.p. 199–200°, was formed during the pyrolyses. This material was produced in very low yield and was isolated by fractional crystallization of the residues from the combined mother liquors remaining after the crystallization of the compound melting at 256–257°. Its infrared spectrum was very similar to that of its isomer, differing only in minor, but unambiguous, respects in the "finger-print" region; the ultraviolet spectra of the two isomers were also very similar but not identical and the compounds exhibited differing solubilities (see Table II). These spectral data, recorded in solution, clearly indicated that the difference between the two isomers was most probably of a stereochemical nature. This relationship was confirmed by the observation that the compound melting at 199–200° gave the phenol IX on acid hydrolysis in like fashion to its isomer. We therefore conclude that the two isomeric pyrolysis products have the stereoisomeric structures XIII and XIIIa.[26] There are no conclusive grounds for the association of a particular isomer with one of the two structures. The fact that the isomer with the higher melting point has the lower solubility and a high wave length band in the ultraviolet which is both more intense and at a longer wave length than that of the low melting isomer indicates that the former may more closely approach planarity than the latter. Of the two structures, XIII and XIIIa, the latter appears the more likely to deviate from planarity because of the steric interactions shown in XIIIb; thus XIIIa may be provisionally assigned as the structure of the lower melting isomer and XIII as that of the isomer, m.p. 256–257°. It must be emphasized, however, that this assignment is tentative, since molecular models fail to show any striking steric effects.

TABLE II

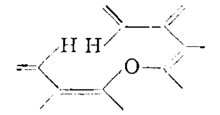
COMPARISON OF THE PROPERTIES OF THE ISOMERIC PYROLYSIS PRODUCTS, $C_{20}H_{12}O_2$ (XIII AND XIIIa)

Property	Major product	Minor product
M.p., °C.	256–257	199–200
Approximate solubility (g./100 ml.) in		
(i) ethyl acetate at 77°	0.2	6.2
(ii) cyclohexane at 80°	0.0	0.6
Ultraviolet max. (mμ (log ε))[a]	214(4.71)	215(4.60)
	278(4.10)	277(4.10)
	354(4.32)	348(4.13)

[a] EtOH solution.



XIIIa



XIIIb

We turn now to the consideration of the mechanism of the formation of XIII and XIIIa. The elegant work of Doering on the decomposition of aliphatic diazo compounds in the presence of hydrocarbons has led him to propose that in a consistent reaction scheme the aliphatic diazo compound absorbs energy with loss of nitrogen to give a carbene which then attacks the hydrocarbon.[27] In most of the cases investigated the necessary energy for the rupture of the C–N bond was supplied by irradiation, but it was shown in the case of the reaction of ethyl diazoacetate with cyclohexane that the same product was obtained in comparable yield by either photolytic or pyrolytic decomposition. A similar parallelism between the courses of these two different modes of decomposition has been observed by Horner,[8] who found that azibenzil on irradiation

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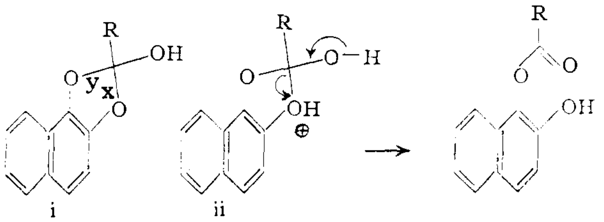
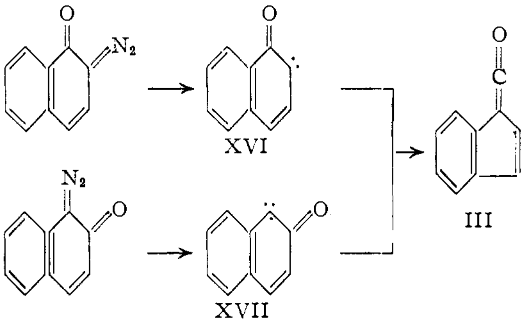
(26) It is noteworthy that in the acid hydrolyses of XIII, XIIIa and XIV only one of the two possible isomeric hydroxyesters was isolated in each case; this was the α-acyloxy-β-hydroxy- compound, rather than the β-acyloxy-α-hydroxy- isomer. Simple equilibration to the more stable product does not appear to be the cause of the selectivity, since the products isolated would be predicted to have the lower stability. The phenomenon is probably due to either (a) equilibration between the two types of product in solution *via* the orthoacid derivative i (*cf.*, S. M. McElvain and M. J. Curry, THIS JOURNAL, **70**, 3781 (1948); A. P. Doerschuk, *ibid.*, **74**, 4202 (1952)) with preferential crystallization of the less soluble product, or (b) more rapid cleavage of bond x than of y *via* ii



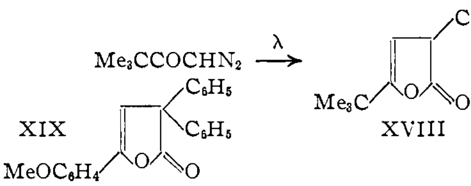
(27) W. von E. Doering and L. H. Knox, THIS JOURNAL, **72**, 2305 (1950); **73**, 828 (1951); **75**, 297 (1953); **78**, 4947 (1956); W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

gives diphenylketene, a product which has long been known to be formed by the thermal decomposition of azibenzil.[28] Thus there are adequate grounds for believing that the first stage of the thermal decomposition of the naphthalenediazoöxides is similar to that of the photolytic decomposition of the *o*-diazoöxides. Since it appears most probable in the latter case that the reaction proceeds by formation of a carbene followed by rearrangement to a ketene,[3,4] we formulate the initial steps in the thermal decomposition of the naphthalenediazoöxides as follows, as has Horner previously[8]

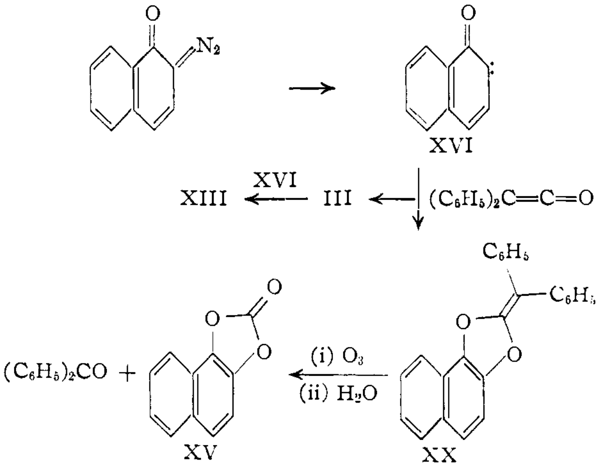


The pyrolysis products XIII and XIIIa could subsequently arise by reaction of the ketene III with either of the unrearranged carbenes, XVI or XVII. The formulation of the course of this reaction in precise terms would be premature, since there is at present no basis for distinguishing between alternative schemes involving concerted and stepwise routes nor between triplet and singlet states for the reacting carbene.[29]

An interesting analogous case of a reaction which probably involves the decomposition of an aliphatic diazo compound to a carbene, rearrangement to a ketene, and subsequent interaction of the ketene and carbene, is to be found in the work of Wiberg,[30] who has observed that photolysis of diazomethyl *t*-butyl ketone gives as the major product 4-hydroxy-2-*t*-butyl-5,5-dimethyl-3-hexenoic acid γ-lactone (XVIII). Kende[31] also has found that irradiation of α-diazo-*p*-methoxyacetophenone in the presence of diphenylketene gives rise to a similar type of product, XIX. In both of these photolytic cases the mode of reaction of the carbene with the ketene is different from that observed in the present study: while addition occurs at the C=C bond of the ketene in the former cases, it occurs at the C=O bond in the present work. Whether this difference represents a dichotomy in the path of photolytic and pyrolytic reactions or of the reactions of diazoöxides and diazoketones remains to be determined.



A corollary of the reaction scheme here proposed is the possibility of the formation of a "mixed" product by pyrolysis of the diazoöxide in the presence of a foreign ketene. This expectation was realized when naphthalene-2,1-diazoöxide was heated in boiling xylene in the presence of diphenylketene. The products included, in addition to the simple pyrolysis product XIII, a colorless compound, $C_{24}H_{16}O_2$, m.p. 130–130.5°, whose infrared spectrum (in CS_2) resembled that of XIII and XIIIa in the presence of bands in the double bond region at 5.91 μ (s) and 6.06 μ (w). Its structure, XX, was proved to be completely analogous to XIII by ozonolysis, which yielded benzophenone and the cyclic carbonate, XV



Experimental[32]

Naphthalene-2,1-diazoöxide.—A procedure, based on that of Bamberger,[33] was used. The yield of material, m.p. 70–75° dec., was 42%. It was best recrystallized in small batches (not greater than 1 g.) from cyclohexane when it was obtained as glistening, yellow plates, m.p. 76–78° dec. (reported m.p. 76°[33]); after a few minutes exposure to daylight it became copper-brown in color and its m.p. fell to 45–65°. Infrared bands ($CHCl_3$): 4.64(w), 4.73, 6.17 μ.

Naphthalene-1,2-diazoöxide.—The procedure of Anderson and Roedel[34] was followed; yield 10%. Infrared bands ($CHCl_3$): 4.69(w), 4.77, 6.17 μ.

Pyrolysis of Naphthalene-2,1-diazoöxide: *trans*- and *cis*-2-Indenylidenenaphtho[1,2]-1,3-dioxoles (XIII and XIIIa).—Naphthalene-2,1-diazoöxide (10.0 g.) was pyrolyzed by the procedure of Horner.[8] At the end of the reflux period, the xylene solution was cooled and placed on a column of Merck alumina (160 g.), packed in benzene. Elution with benzene removed a yellow fraction, which on evaporation yielded 3.04 g. (36%) of pyrolysis product. m.p. 255–257° dec. After five recrystallizations from ethyl acetate it was obtained as long, lemon-yellow needles, m.p. 256–257° dec. (reported m.p. 256°[7,8]). Infrared bands ($CHCl_3$): 5.91, 6.06, 7.88, 10.05, 10.35, 12.12 μ. Ultraviolet spectrum, see Table II.

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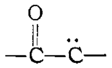
(28) G. Schroeter, *Ber.*, **42**, 2336 (1909).

(29) For, although impressive progress has been made very recently in defining the nature of the simple carbenes, methylene and dibromocarbene (*cf.*, P. S. Skell and R. C. Woodworth, THIS JOURNAL, **78**, 4496 (1956); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956); G. B. Kistiakowsky and K. Sauer, *ibid.*, **78**, 5699 (1956)), little information is available in the case of carbenes of the type:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{C}-$$

(30) K. B. Wiberg and T. W. Hutton, *ibid.*, **76**, 5367 (1954).

(31) A. S. Kende, Ph.D. Thesis, Harvard, 1956.

(32) Melting points were recorded on a Fisher–Johns block and are uncorrected.

(33) E. Bamberger, O. Böcking and E. Kraus, *J. prakt. Chem.*, **105**, 251 (1922).

(34) L. C. Anderson and M. J. Roedel, THIS JOURNAL, **67**, 955 (1945).

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 84.49; H, 4.25. Found: C, 84.52; H, 4.36.

After removal of the yellow fraction with benzene, elution with chloroform removed a red fraction from the chromatographic column; evaporation of this fraction gave a cherry-red glass (1.52 g.) which failed to crystallize (infrared bands at 2.87, 5.86 μ). Subsequent elution with methanol followed by acetic acid gave, in the latter case, a purple fraction which yielded glittering black plates, m.p. > 300° (0.50 g.; infrared bands at 6.24, 6.34, 6.84 μ).

The combined mother liquors from the recrystallization of several preparations of the compound, m.p. 256–257°, were evaporated and the residue (0.36 g., m.p. 192–198°) was fractionally crystallized from ethyl acetate; the other, more soluble, isomer was thus concentrated and was then recrystallized five times from cyclohexane to yield fluffy, pale yellow needles, m.p. 199–200° dec. Infrared bands ($CHCl_3$): 5.91, 6.06, 7.88, 8.95, 10.05, 10.34, 12.11 μ. Ultraviolet spectrum, see Table II.

Anal. Calcd. for $C_{20}H_{12}O_2$: C, 84,49; H, 4.25. Found: C, 84.33; H, 4.19.

Pyrolysis of Naphthalene-1,2-diazoöxide.—A solution of naphthalene-1,2-diazoöxide (0.50 g.) in xylene (20 ml.) was added dropwise under nitrogen to vigorously refluxing xylene (30 ml.). The solution was boiled for 3 hours after the addition was complete, cooled and chromatographed on alumina. The benzene eluate was evaporated and the residue (0.149 g., 32%) was recrystallized five times from ethyl acetate to give lemon-yellow needles, m.p. 255–256° dec., undepressed on admixture with the product, m.p. 256–257°, from naphthalene-2,1-diazoöxide. The infrared and ultraviolet spectra of the two products were identical.

Hydrolysis of XIII. 2-Hydroxy-1-naphthyl 3-Indenecarboxylate (IX).—A mixture of XIII (1.00 g.), acetic acid (40 ml.) and water (8 ml.) was heated until solution was complete. The solution was reduced in volume to 20 ml. by boiling and cooled. After the solution had stood overnight pink crystals separated, were filtered and recrystallized from chloroform, with treatment with activated charcoal. The yield of hydrolysis product, m.p. 182–184° dec., thus obtained was 0.49 g. (46%); additional material could be isolated by concentration of the acetic acid mother liquor. After three recrystallizations from chloroform and two from ethyl acetate the product was obtained as fine, white needles, m.p. 187–189° dec. (reported[8] m.p. 182–183°). Infrared bands (KI disc): 2.96, 5.86, 6.25 μ. Ultraviolet maxima (EtOH): 228 mμ (log ε 4.87), 277 mμ (log ε 3.92), 288 mμ (log ε 3.85), 323 mμ (log ε 3.48), 331 mμ (log ε 3.45).

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.55; H, 4.64.

The hydrolysis product dissolved slowly in 2 *N* aqueous sodium hydroxide to give a dingy blue solution; in methanolic potassium hydroxide the color was royal blue. It dissolved in degassed 2 *N* aqueous sodium hydroxide under nitrogen or in 2 *N* aqueous sodium hydrosulfite to give a clear yellow solution. It was insoluble in 5% aqueous sodium bicarbonate. With ferric chloride and pyridine in chloroform[35] it gave a blue color.

The **methyl ether** of IX was prepared by reaction with ethereal diazomethane and recrystallized from petroleum hexane: m.p. 78–80°. Infrared bands ($CHCl_3$): 5.75, 6.26 μ. Ultraviolet maxima (cyclohexane): 226 mμ (log ε 4.78), 279 mμ (log ε 3.77), 320 mμ (log ε 3.14), 335 mμ (log ε 2.99).

Hydrolysis of XIIIa.—Hydrolysis of the lower melting isomer, XIIIa, using precisely the same procedure as for XIII, gave a product which, after purification, had m.p. 187–188° dec., undepressed by admixture with the hydrolysis product from XIII. The infrared and ultraviolet spectra of the two products were identical.

Hydrogenation of IX. 2-Hydroxy-1-naphthyl 1-Indanecarboxylate (VI). (i) **Over Palladium.**—A solution of IX (0.944 g.) in ethyl acetate (75 ml.) was hydrogenated at atmospheric pressure and room temperature over 10% palladium on charcoal (0.060 g.). Hydrogen uptake ceased after 15 minutes, when 76.6 ml. (1.02 molar equivalents) had been absorbed. Filtration of the catalyst, removal of the solvent and crystallization of the residue from cyclohexane gave the reduced product, m.p. 125–127° (0.670 g., 70%). One recrystallization from cyclohexane followed by four from petroleum-hexane gave small, white rosettes, m.p. 126–127°. Infrared bands ($CHCl_3$): 2.85, 5.69, 6.24 μ. Ultraviolet spectrum, see Table I.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30; for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.73; H, 5.45.

The reduction product dissolved readily in 2 *N* aqueous sodium hydroxide giving a yellow solution; it was insoluble in 5% aqueous sodium bicarbonate. It gave a blue coloration with ferric chloride and pyridine in chloroform.[35]

The **methyl ether**, VIII, of VI (0.40 g.) was prepared by reaction with ethereal diazomethane; distillation of the crude product at 1.5 mm., bath temperature 189–190°, gave the ether (0.34 g., 81%) as a pale yellow oil (reported[8] b.p. 220° (5 mm.)). Infrared bands ($CHCl_3$): 5.69, 6.25 μ. Ultraviolet spectrum, see Table I.

(ii) **Over Nickel.**—A solution of IX (0.257 g.) in ethyl acetate (50 ml.) was hydrogenated at atmospheric pressure and room temperature over reduced sponge nickel (Davison Co.: 0.040 g.). After 4 hours hydrogen absorption had ceased with the uptake of 44.4 ml. (2.13 molar equivalents). Filtration of the catalyst and removal of the solvent gave a pink solid (0.252 g.), m.p. 102–106° (reported[8] for the "tetrahydro" compound, m.p. 110°); it had infrared bands ($CHCl_3$) at 2.85, 5.69 and 5.78 μ. Two recrystallizations from cyclohexane gave material (0.092 g., 36%), m.p. 125–127°. This product showed no mixed melting point depression with that from the hydrogenation over palladium and the infrared and ultraviolet spectra of the two products were identical.

Basic Hydrolysis of VI.—A suspension of VI (0.100 g.) in water (30 ml.) was treated with a solution of sodium carbonate (0.30 g.) in water (20 ml.); the water used had previously been degassed and all operations were carried out under nitrogen. The mixture was stirred for 6 hours at room temperature and then treated with 2 *N* hydrochloric acid (10 ml.). It was extracted with ethyl acetate and the extract was in turn extracted with 5% aqueous sodium bicarbonate. The ethyl acetate layer was washed with water containing a little sodium hydrosulfite, dried and freed of solvent. The residue was sublimed at 2 mm., bath temperature 100°, to give **1,2-naphthalenediol** (0.032 g., 61%), m.p. 107–109° dec., undepressed on admixture with authentic 1,2-naphthalenediol,[36] m.p. 109–110° dec. The infrared spectra of the degradative and authentic samples were identical; bands ($CHCl_3$): 2.86, 3.10, 6.11, 6.24 μ.

The aqueous bicarbonate extract was acidified and extracted with ether. The ethereal extract was dried and freed of solvent. The residue was sublimed at 2 mm., bath temperature 100°, to give **1-indanecarboxylic acid** (0.051 g., 91%), m.p. 52–57°, which after one recrystallization from petroleum hexane melted at 58–59°, undepressed on admixture with a sample of 1-indanecarboxylic acid, m.p. 59–60°, prepared by hydrogenation of 3-indenecarboxylic acid (*vide infra*) over platinum (reported[19] m.p. 57–58°). The infrared spectra of the degradative and authentic samples were identical; bands ($CHCl_3$): 3–4, 5.85 μ.

Base Hydrolysis of IX.—A solution of IX (0.174 g.) in 2 *N* aqueous sodium hydroxide (50 ml.) containing sodium hydrosulfite (0.10 g.) was allowed to stand at room temperature for 5 hours under nitrogen. The solution was then acidified and separated into neutral, phenolic, and acidic fractions in the customary manner. The acidic fraction yielded, after recrystallization from benzene, **3-indenecarboxylic acid** (0.028 g., 30%), m.p. 157–159° dec., undepressed by admixture with authentic 3-indenecarboxylic acid; the infrared spectra of the degradative and authentic samples were identical. The phenolic fraction (0.080 g.) yielded a brown tar which resisted purification; the neutral fraction contained only sulfur.

3-Indenecarboxylic Acid.—A procedure patterned after that of Knowles, Kuck and Elderfield[19] was used. Sodium (4.5 g.) was added to a solution of freshly distilled indene (38 ml.) and pyridine (1 ml.) in purified dioxane (75 ml.). After 7 hours reflux, the clear red solution was poured over Dry Ice (450 g.). After the mixture had come to room temperature it was partitioned between 4 *N* hydrochloric acid (300 ml.) and ether (200 ml.), and the ether layer was extracted with 1 *N* aqueous sodium hydroxide (200 ml.). Acidification of the basic solution precipitated the crude

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(35) S. Soloway and S. H. Wilen, *Anal. Chem.*, **24**, 979 (1952).

(36) Prepared by the method of L. F. Fieser and M. Fieser, THIS JOURNAL, **56**, 1575 (1934); **57**, 493 (1935).

product, which was filtered, washed with water, dried *in vacuo* over calcium chloride, and recrystallized from benzene to give 3-indenecarboxylic acid (19.8 g., 64%), m.p. 158–160° dec. (reported[19] m.p. 159.5–161°). Infrared bands ($CHCl_3$): 3–4, 5.90, 6.26, 6.36 μ.

Hydrazinolysis of VIII.—A solution of VIII (0.308 g.) in absolute ethanol (1.22 g.) was treated with 85% hydrazine (0.20 g.). The mixture was heated under reflux for 4 hours and then stored at 0° for three days. The crystalline **1-indanecarboxhydrazide** (0.065 g.), m.p. 126–127° dec. (reported[8] m.p. 128°), which had separated was filtered and the mother liquor, was diluted with ether and extracted with 2 *N* hydrochloric acid. The acid extract was neutralized with aqueous sodium bicarbonate and extracted with ether; the ethereal extract was washed with water, dried and freed of solvent to yield further hydrazide (0.037 g.), m.p. 125–127° dec. The total yield of hydrazide was 0.102 g. *i.e.*, 60%, based on the formation of one molar equivalent. Infrared bands ($CHCl_3$): 2.95, 3.04, 6.01, 6.16 μ.

The ethereal solution remaining after the extraction with hydrochloric acid was washed with a dilute aqueous solution of sodium hydrosulfite, dried and freed of solvent. The residue was sublimed at 1 mm., bath temperature 50°, and the sublimate was resublimed at atmospheric pressure, bath temperature 100°, to give 2-methoxy-1-naphthol as transparent plates, m.p. 73–75°.[37] This gave a green color with ferric chloride and pyridine in chloroform[35]; infrared bands ($CHCl_3$): 2.86, 6.12, 6.24 μ; ultraviolet maxima (EtOH): 230 mμ (log ϵ 4.82), 280 mμ (log ϵ 3.58), 290 mμ (log ϵ 3.53), 332 mμ (log ϵ 3.32). A solution of the crude product (0.050 g) in 0.1 *N* aqueous sodium hydroxide (9 ml.) was treated with benzoyl chloride (0.10 g.). The mixture was shaken for 10 minutes and then extracted with benzene. The extract was washed with dilute aqueous sodium hydroxide and with water, dried and freed of solvent. The residue on crystallization from petroleum–hexane gave **2-methoxy-1-naphthyl benzoate** as square, transparent prisms, m.p. 107–108° (reported[18] m.p. 110°). Infrared bands ($CHCl_3$): 5.75, 6.10(w), 6.25, 6.35 μ. Ultraviolet maxima (EtOH): 227 mμ (log ϵ 4.80), 274 mμ (log ϵ 3.88), 321 mμ (log ϵ 3.17).

Hydrogenation of XIII. 2-(1-Indanylidene)-naphtho[1,2]-1,3-dioxole (XIV). (i) **Over Palladium.**—A suspension of XIII (0.247 g.) in ethyl acetate (100 ml.) was hydrogenated at atmospheric pressure and room temperature over 10% palladium on charcoal (0.035 g.). After 45 minutes hydrogen absorption had ceased; the total uptake was 21.4 ml. (1.01 molar equivalents). After filtration of the catalyst and removal of solvent, the crude product was crystallized from cyclohexane to give reduction product (0.189 g., 77%), m.p. 198–199° dec. Five recrystallizations from cyclohexane gave lemon-yellow needles, m.p. 199–201° dec. Infrared bands (CCl_4): 5.80, 6.83, 7.83, 10.07, 10.47 μ. Ultraviolet maxima (cyclohexane): 218 mμ (log ϵ 4.73), 288 mμ (log ϵ 4.34), 326 mμ (log ϵ 4.12), 356 mμ (log ϵ 3.67).

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93; for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.78; H, 5.04.

(ii) **Over Nickel.**—A suspension of XIII (0.303 g.) in ethyl acetate (100 ml.) was hydrogenated at atmospheric pressure and room temperature over reduced sponge nickel (Davison Co., 0.040 g.). After 7 minutes one molar equivalent of hydrogen had been absorbed; after 45 minutes absorption had ceased with a total uptake of 48.1 ml. (1.87 molar equivalents). After filtration of the catalyst and removal of solvent the crude product, m.p. 176–192°, was crystallized from cyclohexane to give product (0.187 g., 61%), m.p. 196–198° dec., undepressed by admixture with the product from hydrogenation over palladium. The infrared spectra of the two products were identical.

Hydrolysis of XIV.—The dihydro compound XIV (0.098 g.) was dissolved in a boiling mixture of acetic acid (5 ml.) and water (0.5 ml.). After cooling, the solution was poured into water (20 ml.) and then extracted with ethyl acetate. The extract was dried and freed of solvent to give crude product (0.078 g., 75%), m.p. 113–117°. Recrystallization from cyclohexane gave material, m.p. 125–126°, undepressed on admixture with 2-hydroxy-1-naphthyl 1-indanecarboxylate (VI) obtained by the hydrogenation of IX. The infrared spectra of the two samples were identical.

Attempted Reduction of XIII with Zinc.—A solution of XIII (0.100 g.) in ethanol (50 ml.) was refluxed with zinc dust (1.0 g.) for 24 hours. Filtration of the zinc and removal of the solvent left a residue (0.093 g.), m.p. 245–253° dec., whose infrared spectrum was essentially that of XIII. No reaction was observed also when XIII was refluxed in xylene with activated zinc[38] for 48 hours.

Ozonolysis of XIV.—A solution of XIV (0.384 g.) in ethyl acetate (50 ml.) was cooled to −78° and treated with a stream of ozonized oxygen for 2 minutes, when the yellow color had disappeared and a faint blue color was apparent. Nitrogen was then bubbled through the solution until the odor of ozone could no longer be detected. Water (50 ml.) was added and the mixture was allowed to stand at room temperature for 12 hours. The ethyl acetate layer was separated, washed with water, dried and freed of solvent. The crude residue was extracted with boiling cyclohexane (8 ml.); the insoluble residue (0.036 g.) was identified on the basis of its infrared spectrum as phthalic acid. From the cooled cyclohexane extract there separated colorless crystals of **1,2-naphthalenediol carbonate** (0.114 g., 46%), m.p. 136–137°, undepressed by admixture with an authentic sample (*vide infra*); the infrared spectra of the ozonolytic product and the authentic sample were identical.

The cyclohexane mother liquor from crystallization of the carbonate was concentrated and placed on a column of alumina (1 g.) packed in cyclohexane. Elution with cyclohexane (25 ml.) gave a low-melting (*ca.* 35°) solid whose infrared spectrum was identical to that of **1-indanone**; the yield was 0.090 g. (51%). Its identity was confirmed by the preparation by the usual methods of a **2,4-dinitrophenylhydrazone**, m.p. 257–258°, and **semicarbazone**, m.p. 231–233° dec., whose melting points showed no depression on admixture with samples of the corresponding derivatives prepared from authentic 1-indanone (reported m.p.'s 258°,[39a] 265°[39b] and 235° dec.,[40a] 247°,[40b] respectively).

1,2-Naphthalenediol Carbonate (XV).—A procedure similar to that used for the preparation of catechol carbonate[41] was employed. Phosgene was bubbled into a solution of freshly recrystallized 1,2-naphthalenediol (8.5 g.) in pyridine (50 ml.), cooled in an ice-bath, until 6.0 g. had been absorbed. The mixture was heated at 90° for 3 hours, and then poured on to ice. The precipitate was filtered and dissolved in ether. The ethereal solution was washed with 2 *N* aqueous sodium hydroxide and with water, dried and freed of solvent. The residue was crystallized from benzene, with charcoal treatment, to give the carbonate (5.5 g., 56%), m.p. 136–137.5°. Three recrystallizations from cyclohexane afforded long, white needles, m.p. 138–139°. Infrared bands ($CHCl_3$): 5.38, 5.48, 6.83, 7.88 μ.

Anal. Calcd. for $C_{11}H_6O_3$: C, 70.97; H, 3.25. Found: C, 70.88; H, 3.38.

Reaction of Naphthalene-2,1-diazoöxide with Diphenylketene. 2-Benzohydrylidenenaphtho[1,2]-1,3-dioxole (XX).—A solution of freshly distilled diphenylketene[42] (2.00 g.) and naphthalene-2,1-diazo-oxide (2.00 g.) in dry xylene (140 ml.) was refluxed for 30 minutes, when the evolution of nitrogen was complete. The solution was concentrated under reduced pressure on the steam-bath to *ca.* 15 ml., cooled, and filtered from some XIII which crystallized at this point. The filtrate was placed on a column of Merck alumina (50 g.) packed in cyclohexane. The column was eluted with cyclohexane (250 ml.), followed by benzene (250 ml.). The colorless cyclohexane eluate on evaporation gave an oil (1.11 g.) which crystallized after standing for several days to a colorless solid, m.p. 126–128°. Three recrystallizations from cyclohexane gave XX as clustered, white needles, m.p. 130–130.5°. Infrared bands (CS_2): 5.91, 6.06, 7.81, 9.97, 10.50 μ. Ultraviolet maxima (cyclohexane): 218 mμ (log ϵ 4.88), 290 mμ (log ϵ 4.49), 322 mμ (log ϵ 4.09), 355 mμ (log ϵ 3.76).

Anal. Calcd. for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.67; H, 4.68.

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(37) *Cf.*, the m.p. of 91° reported for 1-methoxy-2-naphthol: H. Bezdzik and P. Friedlaender, *Monatsh.*, **30**, 281 (1909); E. Bamberger and S. Wildi, *J. prakt. Chem.*, **105**, 278 (1922).

(38) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4236 (1952).

(39) (a) C. F. H. Allen, *ibid.*, **52**, 2955 (1930); (b) R. Seka and W. Kellermann, *Ber.*, **75**, 1730 (1942).

(40) (a) H. Leuchs and G. Kowalski, *ibid.*, **58**, 2288 (1925); (b) B. Tchoubar, *Compt. rend.*, **214**, 117 (1942).

(41) S. Peterson in Houben-Weyl "Methoden der Organischen Chemie," Georg Thieme Verlag, Stuttgart, 1952, Vol. VIII, p. 109.

(42) Kindly supplied by Dr. A. S. Kende.

The yellow benzene eluate from the chromatographic separation yielded, on removal of solvent, further XIII which, combined with that which had crystallized previously, weighed 0.51 g., m.p. 249–253° dec.

Ozonolysis of XX.—A solution of XX (0.200 g.) in ethyl acetate (50 ml.), cooled to −78°, was treated with ozonized oxygen for 2 minutes, when the solution had become blue. Excess ozone was swept out with nitrogen, water (50 ml.) was added, and, after the mixture had stood at room temperature overnight, the ethyl acetate layer was separated, dried and freed of solvent. The residue was dissolved in boiling cyclohexane (5 ml.). On cooling the solution, **1,2-naphthalenediol carbonate** (0.072 g., 65%), m.p. 135–137°, crystallized. It was identified by the identity of its infrared spectrum with that of the authentic compound, and by its failure to depress the m.p. of the latter. The cyclohexane mother liquor was placed on a column of Merck alumina (1.0 g.), which was then eluted with cyclohexane (25 ml.). Removal of solvent from the eluate gave a low-melting solid (m.p. *ca.* 40°) whose infrared spectrum was identical with that of **benzophenone**; the yield was 0.065 g. (60%). Its identity was confirmed by the preparation of a **2,4-dinitrophenylhydrazone**, m.p. 243.5–244°, undepressed by admixture with authentic benzophenone 2,4-dinitrophenylhydrazone (reported m.p. 240–241°[43]).

Acknowledgment.—We gratefully acknowledge fellowship support from the National Heart Institute of the National Institutes of Health and a grant from the Mallinckrodt Chemical Works which helped in defraying the expenses of this investigation.

[43] J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946).

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[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Preparation and Reactions of α,α'-Dibromo-α,α'-dinitrocyclic Ketones[1]

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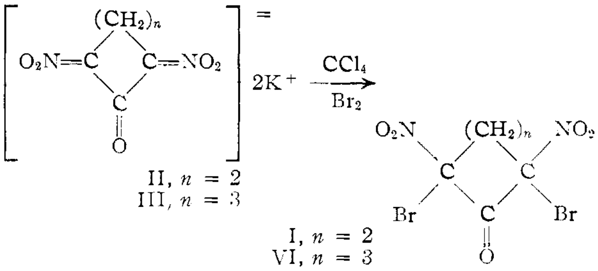
α,α'-Dinitro-α,α'-dibromocyclic ketones, such as α,α'-dinitro-α,α'-dibromocyclopentanone (I), α,α'-dinitro-α,α'-dibromocyclohexanone and β-nitro-β-bromo-α-tetralone were prepared by bromination of the corresponding potassium salts of dinitrocyclic and mononitrocyclic ketones. I was converted to 1,1,4,4-tetrabromo-1,4-dinitrobutane on treatment with aqueous base or acid. Refluxing of I with methanolic hydrogen chloride gave dimethyl 2-bromo-2-nitroglutarate and methyl 2,5-dibromo-2,5-dinitropentanoate, respectively.

The reactions of the salts of α,α'-dinitrocyclic ketones have been little investigated. Wieland[2] reported that careful acidification with mineral acid of the dipotassium salts of α,α'-dinitrocyclopentanone (II) and α,α'-dinitrocyclohexanone (III) gave first the mono-salts and then the free dinitroketones. Klager[3] has shown that the only identifiable products from the reaction of compounds II and III with bromine in either neutral or basic aqueous media are $\alpha,\alpha',\omega,\omega'$-tetrabromo-$\alpha,\omega$-dinitroparaffins (IV). It now has been found that ring opening also occurs in acidic medium, for a 10% yield of 1,1,4,4,-tetrabromo-1,4-dinitrobutane (V) was obtained when II reacted with bromine in an excess of acetic acid.

In order to obtain more insight into this reaction, the synthesis of α,α'-dinitro-α,α'-dibromocyclic ketones was undertaken, since they were considered possible intermediates in the ring opening reaction leading to IV. It was likely that ring opening during the bromination might be avoided under strictly anhydrous conditions. When compounds II and III were dried carefully at 50° and 2 mm. over concd. sulfuric acid and then brominated in carbon tetrachloride, α,α'-dibromo-α,α'-dinitrocyclopentanone (I) and α,α'-dibromo-α,α'-dinitrocyclohexanone (VI) were obtained as solids in yields of 71 and 25%, respectively.

When incompletely dry salts were used some ring opening occurred with formation of IV.

After several recrystallizations from carbon tetrachloride, compound I melted from 122–125° depending on the rate of heating. This can be attributed to the fact that the compound may exist as a mixture of *meso*-form and *d,l*-pair. Five crystallizations with hexane yielded a solid which melted sharply at 124–125°. However, this solid as well as the mixture slowly converted at room temperature to V. Compound VI was obtained in two forms, an unstable oil which liberated bromine and a stable crystalline compound (m.p. 134–135°). Since the infrared spectrum (*vide infra*) of solid VI seems to indicate that it is the *meso*-form, the unstable oil is probably the *d,l*-pair.



II, $n = 2$
III, $n = 3$

I, $n = 2$
VI, $n = 3$

The structure of compounds I and VI was established by (1) elemental analysis, (2) infrared spectra and (3) reactions which caused ring opening. The infrared spectrum of I showed the characteristic absorption maximum for the C=O group at 5.65 μ. The maxima of the NO_2 group at 6.35 μ (asymmetric stretching) and 7.40 μ (symmetric stretching) were shifted, and this was also found in the spectrum of compound VI (6.36 and 7.42 μ). These findings agree with the observations of J. F. Brown,[4] who found that negative groups such as bromine cause a shift of the asymmetric

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[1] (a) From the Ph.D. thesis of James W. Shepherd, Purdue University, 1954; (b) presented before the Division of Organic Chemistry at the Dallas Meeting of the American Chemical Society, April, 1956.

[2] H. Wieland, P. Garbsch and J. J. Chavin, *Ann.*, **461**, 295 (1928).

[3] K. Klager, *J. Org. Chem.*, **20**, 646 (1955).

[4] J. F. Brown, THIS JOURNAL, **77**, 6341 (1955).