Harvey (Ben May Laboratory, University of Chicago) and Professor William Closson (State University of New York at Albany, N. Y.). We are also indebted to the chemistry department of the California Institute of Technology for running the mass spectra.

Dipolar and Carbenic Reactions of *p*-Diazooxides

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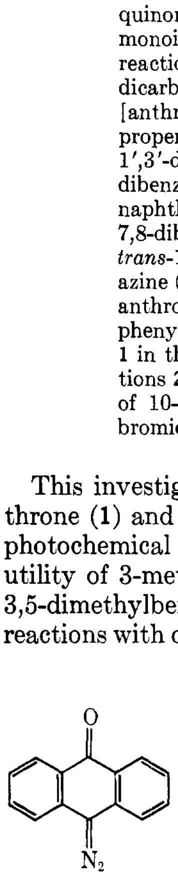
10-Diazoanthrone (**1**) has been prepared by base-catalyzed decomposition of 9,10-anthraquinone mono-*p*-tosylhydrazone (**8**), by oxidation of 9,10-anthraquinone monohydrazone (**7**), and by amination of 9,10-anthraquinone monoxime (**9**). Reactions of **1** with acrylonitrile, methyl vinyl ketone, methyl methacrylate, *trans*-1,2-dibenzoylethylene, and *p*-benzoquinone yield spiro[anthrone-10,1′-cyclopropanes] (**12–15**, **18**); with *p*-benzoquinone, 4′,7′-dihydroxyspiro[anthrone-10,3′-indazole] (**17**) is also obtained. N-Phenyl-9,10-anthraquinone monoimine N-oxide (**19**) and N,N-dicarbethoxy-9,10-anthraquinone monohydrazone (**20**) are formed from reactions of **1** with nitrosobenzene and with diethyl azodicarboxylate. Additions of **1** to dimethyl acetylenedicarboxylate and to benzyne give 4′,5′-dicarbomethoxyspiro[anthrone-10,3′(3′H)-pyrazole] (**21**) and spiro[anthrone-10,3′-indazole] (**23**). Photolysis of **21** results in 1′,2′-dicarbomethoxyspiro[anthrone-10,3′-cyclopropene] (**22**). Thermolysis of **1** in 9,10-phenanthrenequinone yields spiro[anthrone-10,2′-(phenanthro[9.10]-1′,3′-dioxole)] (**24**) and $\Delta^{10,10'}$-bianthrone (**26**). 3-Methylnaphthalene 1,4-diazooxide (**2**) adds to *trans*-1,2-dibenzoylethylene and to benzyne to form *trans*-2,3-dibenzoyl-2′-methylspiro[cyclopropane-1,4′-(1′[1′H,4′H]-naphthalenone)] (**27**) and 2′-methylspiro[indazole-3,4′-(1′[1′H,4′H]-naphthalenone)](**28**). 3,5-Dimethyl-*trans*-7,8-dibenzoylspiro[2.5]octa-2,5-dien-4-one (**29**) is obtained from 3,5-dimethylbenzene 1,4-diazooxide (**3**) and *trans*-1,2-dibenzoylethylene. Thermolysis of **1** in benzene catalyzed by copper affords 9,10-anthraquinone azine (**30**) and **26**. Photolysis of **1** in benzene produces biphenyl (**35**), 10,10′-bianthrone (**36**), **30**, and 10-phenylanthrone (**37**). Decomposition of **1** in mesitylene yields **36** and 10,10-bis(3,5-dimethylbenzyl)anthrone. Triphenylphosphine reacts with **1**, yielding 9,10-anthraquinone monotriphenylphosphazine (**39**). Photolysis of **1** in the presence of triphenylphosphine leads to 10-triphenylphosphoranylanthrone (**38**); under similar conditions **2** and triphenylphosphine give 2-methyl-1,4-naphthoquinone 4-triphenylphosphazine (**40**). Displacement of 10-bromoanthrone by triphenylphosphine results predominantly in anthracene-9-oxytriphenylphosphonium bromide (**42**). Both *m*- and *p*-nitrobenzaldehyde react with **38** to give benzylideneanthrones (**44a** and **44b**).

This investigation involves synthesis of 10-diazoanthrone (**1**) and elaboration of its addition, thermal and photochemical reactions, and demonstration of the utility of 3-methylnaphthalene 1,4-diazooxide[2] (**2**) and 3,5-dimethylbenzene 1,4-diazooxide[2] (**3**) in 1,3-dipolar reactions with olefins and acetylenes.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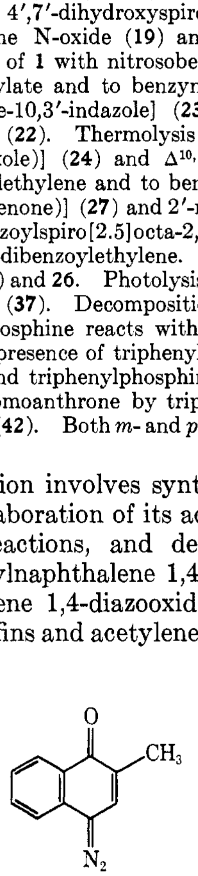

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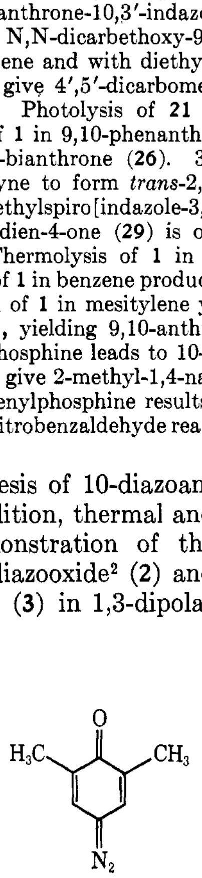

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Presently **1** has been prepared from 9,10-anthraquinone monohydrazone (**7**), 9,10-anthraquinone mono-*p*-tosylhydrazone (**8**), and 9,10-anthraquinone monooxime (**9**), respectively. Neither **7** nor **8** is readily obtainable from 9,10-anthraquinone and hydrazine or *p*-tosylhydrazine in methanol containing hydrogen chloride. Monohydrazone **7** is formed (40%) along with 10-bromo-10,10′-bianthrone (**6**) from 10,10-dibromoanthrone (**4**) and hydrazine possibly as in eq 1 and 2[3] (Scheme I). Oxidation of **7** by mercuric oxide gives **1** ($\sim$100%). Mono-*p*-tosylhydrazone **8** is preparable from 10,10-dibromoanthrone (**4**) and *p*-tosylhydrazine and then converted (98%) by sodium hydroxide into **1** (eq 3).

9,10-Anthraquinone monooxime (**9**) and chloramine in basic solution yield **1**. Another principle product is 9,10-anthraquinone monoimine (**11**). Imines have not been reported in Forster reactions of oximes with chloramine.[4] Carbon amination of 9,10-anthraquinone monooxime anion to **10** and loss of water or nitroxyl (HNO; as nitrous oxide and water, eq 4) account for **1** and **11** though other mechanisms may be involved.[4b,5]

Diazooxides **2** and **3** were prepared[2] by reactions of 2-methyl-1,4-naphthoquinone and of 2,6-dimethyl-1,4-benzoquinone with *p*-tosylhydrazine and subsequent base-catalyzed decomposition.

Decomposition of **1** occurs slowly in refluxing benzene. The diazooxide functions as a 1,3-dipolar reagent with extrusion or retention of nitrogen upon addition to electron-deficient or strained olefins and acetylenes. Thus reactions of **1** with acrylonitrile, methyl vinyl ketone, methyl methacrylate, and *trans*-1,2-dibenzoylethylene take place in hot benzene with loss of nitrogen to give the spiro[anthrone-10,1′-cyclopropanes], **12–15** (56–91%).[6] The structures of the adducts as spiro-

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[1] (a) Abstracted in part from the Ph.D. dissertation of J. C. Fleming, The Ohio State University, Columbus, Ohio, 1964. (b) *Dissertation Abstr.*, **25**, 6958 (1965).

[2] W. Ried and R. Dietrich, *Ber.*, **94**, 387 (1961).

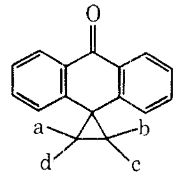
[3] (a) Reduction of positive halogen by hydrazine is well documented[3b] and 10-bromoanthrone (**5**) is converted into **6** by amines.[3c] (b) C. C. Clark, "Hydrazine," Mathieson Chemical Corp., Baltimore, Md., 1953, p 103. (c) E. B. Barnett, J. W. C. Cook, and H. H. Grainger, *J. Chem. Soc.*, **121**, 2059 (1922).

[4] (a) See B. Eistert, M. Regitz, G. Heck, and H. Schwall, "Methoden Der Organischen Chemie," E. Müller, Ed., G. Thieme Verlag, Stuttgart, Vol. X, part 4, 1968, pp 582-587 and references therein. (b) J. Meinwald, P. G. Gassman, and E. G. Miller, *J. Amer. Chem. Soc.*, **81**, 475 (1959).

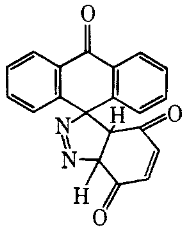
[5] (a) M. Regitz, *Ber.*, **97**, 2742 (1964), prepared **1** (94%) from anthrone, *p*-tosyl azide, and piperidine. (b) For additional physical properties of **1**, see G. Cauquis, G. Reverdy, and R. M. Rastoldo, *Compt. Rend.*, **260**, 2259 (1965).

[6] Spiro[anthrone-10,1′-cyclopropanes] have been prepared from 10-methyleneanthrones and diazo compounds by A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).

cyclopropanes rather than as isomers[1,7] are indicated by their lack of color, their absorption spectra for appropriate carbonyl groups and no hydroxyl functions, and their nmr properties for cyclopropyl hydrogen (see Experimental Section). On the basis of the initial stereochemistry of the 1,2-dibenzoylethylene as *trans*, considerations of reaction mechanism, and the stereochemical result for reaction of **2** and *trans*-1,2-dibenzoylethylene, **15** is probably of *trans* structure.



12a,b,c = H; d = CN
13a,b,c = H; d = $COCH_3$
14a,d = H; b = CH_3; c = CO_2CH_3
15a,c = H; b,d = COC_6H_5



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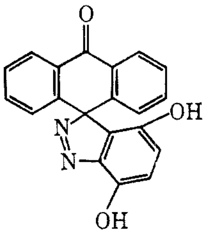

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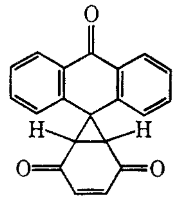

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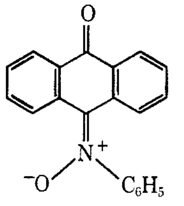

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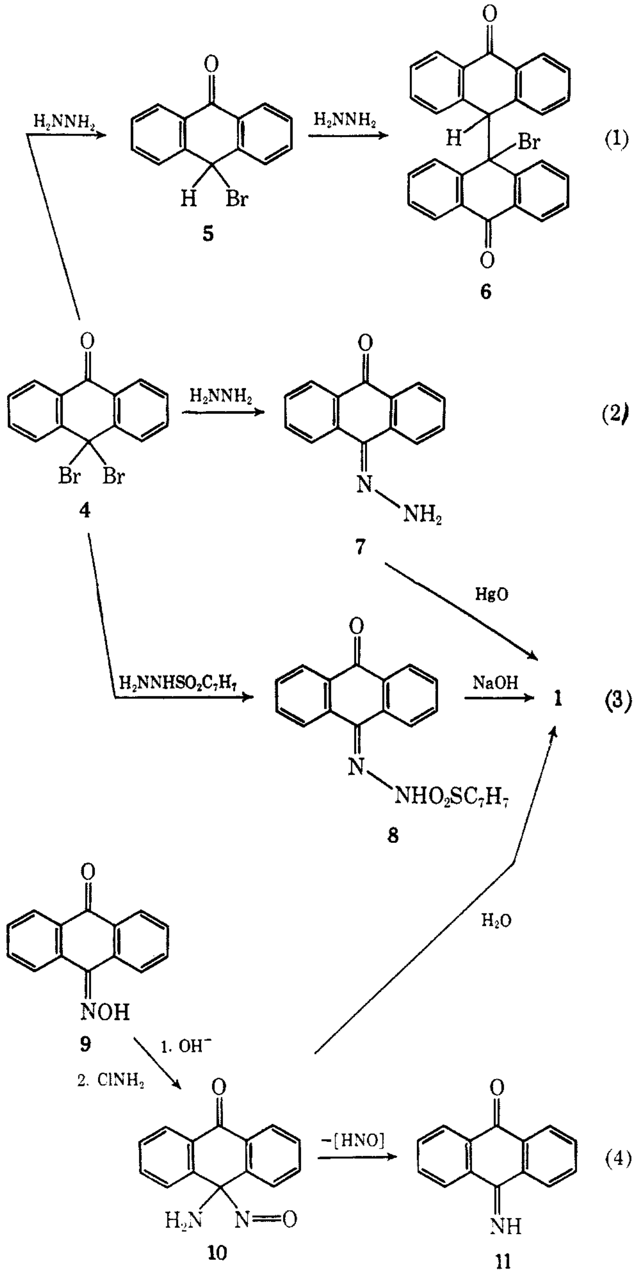
1 reacts with *p*-benzoquinone at 25° with incorporation of nitrogen to give the thermally stable spiroindazole **17** and with extrusion of nitrogen to yield the spirocyclopropane **18**. At elevated temperatures conversion of **1** and *p*-benzoquinone into **18** is increased. The structure of **18** is established by its carbonyl doublet centered at 6.0 μ and its nmr absorption for singlets at τ 6.77 (area 2, cyclopropyl hydrogens) and 3.37 (area 2, vinyl hydrogens) and aromatic multiplets (area 8). The dipolar adduct **16** may account for **17** upon enolization and for **18** by loss of nitrogen. The present results are analogous to a previous report[8] that 9-diazofluorene reacts with *p*-benzoquinone, 1,4-naphthoquinone, and quinizarinquinone to yield indazoles and minor "nitrogen free" products. Though the minor adducts were described (empirical formulas, color, ketonic, etc.), their structures were not assigned. It is probable that the unidentified products[8] are cyclopropanes similar to **18**.

Addition of **1** to nitrosobenzene occurs at 25° with loss of nitrogen to give N-phenyl-9,10-anthraquinone monoimine N-oxide (**19**, 72%, yellow). The product is assigned as a nitrone rather than as an oxazirane because of its color, its spectra, its thermal stability and by analogy with formation of nitrones[9] from reactions of diphenyldiazomethane and of 9-diazofluorene with nitrosobenzene.

Reaction of **1** with diethyl azodicarboxylate proceeds in refluxing benzene to form N,N-dicarbethoxy-9,10-anthraquinone monohydrazone (**20**, 72%, yellow crystals). The structure of the reaction product is designated as **20** (eq 5) because of its color; its ethyl groups are nuclear magnetically equivalent (a single ethyl pattern consisting of a methylene quartet at τ 5.82 and a methyl triplet at 8.87), and its hydrolysis to 9,10-anthraquinone. The reaction of **1** and diethyl azodicarboxylate is related to that of 9-diazofluorene and diethyl azodicarboxylate in that 4′-carbethoxy-2′-ethoxyspiro[fluorene-9,5′-(1′,3′,4′[4′H,5′H]-oxadiazole)] is formed as an isolable intermediate which then rearranges at 50° to fluorenone N,N-dicarbethoxyhydrazone.[10]

Scheme I



4′,5′-Dicarbomethoxyspiro[anthrone-10,3′(3′H)-pyrazole] (**21**, 64%) is formed rapidly from **1** and dimethyl acetylenedicarboxylate in benzene at 20–30.° Pyrazole **21** photolyzes in ether with loss of nitrogen to give 1′,2′-dicarbomethoxyspiro[anthrone-10,3′-cyclopro-

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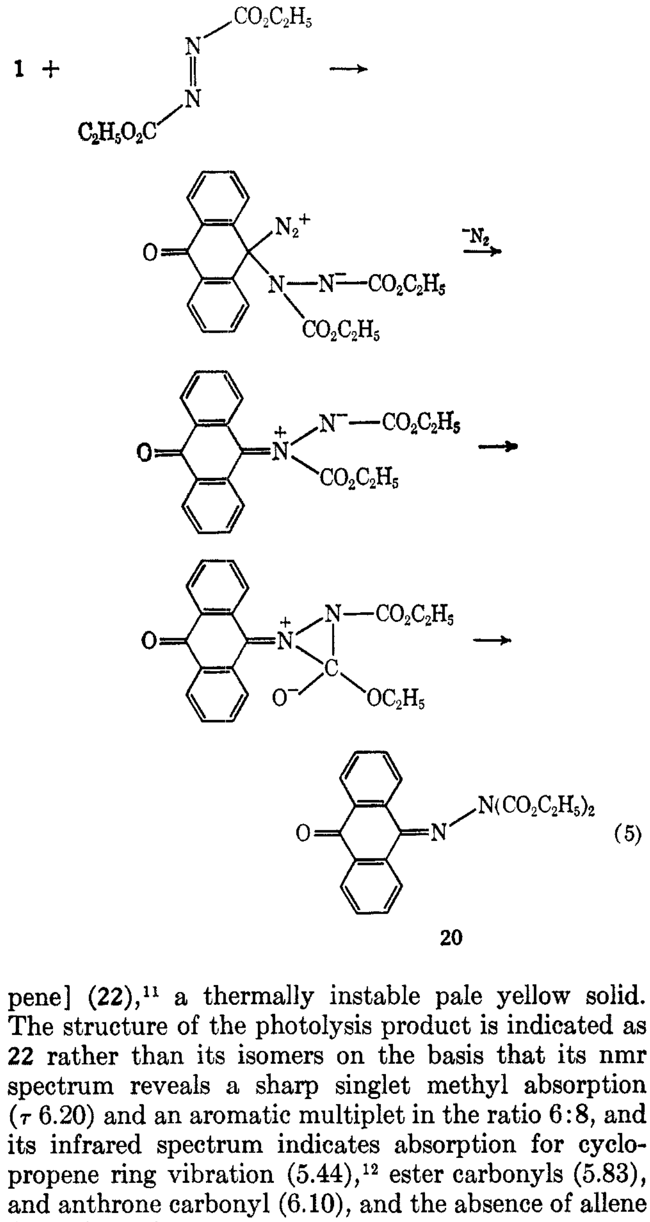
[7] (a) Photochemical isomerization of spiro[2,5]octa-2,5-dien-4-one has been reported by D. I. Schuster and C. J. Polowczyk, *J. Amer. Chem. Soc.*, **88**, 1722 (1966). (b) Adducts **12–15** are thermally instable; the products of their decompositions have not been determined.

[8] L. Horner and E. Lingnau, *Ann. Chem.*, **591**, 21 (1955).

[9] A. W. Johnson, *J. Org. Chem.*, **28**, 252 (1963).

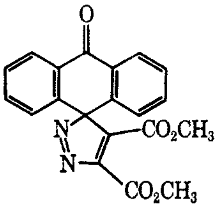
[10] E. Fahr, K. Döppert, and F. Scheckenbach, *Ann. Chem.*, **696**, 139 (1966), and references therein.



(5)

20

pene] (22),[11] a thermally instable pale yellow solid. The structure of the photolysis product is indicated as 22 rather than its isomers on the basis that its nmr spectrum reveals a sharp singlet methyl absorption (τ 6.20) and an aromatic multiplet in the ratio 6:8, and its infrared spectrum indicates absorption for cyclopropene ring vibration (5.44),[12] ester carbonyls (5.83), and anthrone carbonyl (6.10), and the absence of allene (5.13 μ) and hydroxyl groups.



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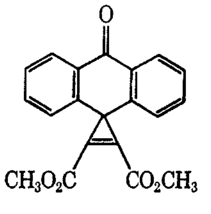

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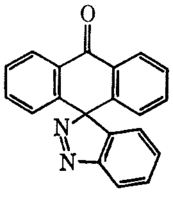
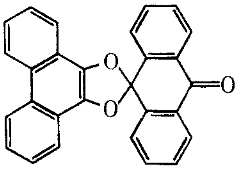


23

Benzyne adds (87%) to 1 to produce spiro[anthrone-10,3′-indazole] (23).[13,14] Photolysis of 23 results in loss of nitrogen but the products have not been identified.

9,10-Phenanthrenequinone reacts with 1 in refluxing benzene to form dioxole 24 (35%) along with $\Delta^{10,10'}$-bianthrone (26). The possibility that the phenanthrenequinone capture product is the isomeric keto-epoxide (25)[15] is ruled out on the basis of its infrared



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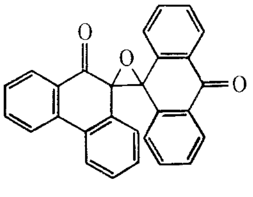

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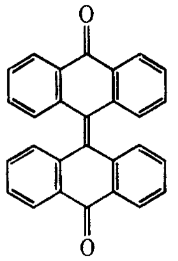
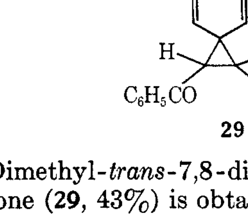


26

spectrum. Two distinct carbonyl absorptions should occur in 25, the anthrone carbonyl should absorb above 6 μ and that of the phenanthrone moiety below 6 μ. Adduct 24 however exhibits sharp absorption at 6.01 μ. $\Delta^{10,10'}$-Bianthrone (26) is probably formed *via* carbenic coupling as in subsequent examples.

Study has been initiated of the reactions of 2 and 3 with representative olefins and acetylenes. Addition of 2 to *trans*-1,2-dibenzoylethylene in 1 week at 20–30° yields *trans*-2,3-dibenzoyl-2′-methylspiro[cyclopropane-1,4′-(1′[1′H,4′H]-naphthalenone)] (27, 84%). The stereochemistry of 27 is *trans* on the basis of nonequivalence of its cyclopropyl hydrogens as derived from the nmr quartet centered at τ 5.54. Benzyne reacts with 2 giving 2′-methylspiro[indazole-3,4′-(1′[1′H,4′H]-naphthalenone)] (28, 47%), a photosensitive product.



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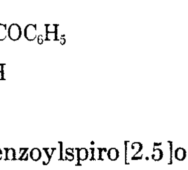

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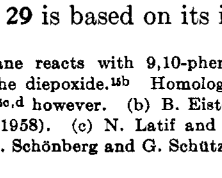

29

3,5-Dimethyl-*trans*-7,8-dibenzoylspiro[2.5]octa-2,5-dien-4-one (29, 43%) is obtained from 3 and *trans*-1,2-dibenzoylethylene in benzene for 4 weeks at 20–30°. The structure of 29 is based on its infrared absorption

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(11) (a) Photolyses of 3H-pyrazoles and indazoles have been utilized previously to produce cyclopropenes and benzocyclopropenes and isomers thereof. (b) G. L. Closs, W. A. Boll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, **90**, 173 (1968). (c) G. Ege, *Tetrahedron Lett.*, 1667 (1963). (d) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 526 (1964). (f) G. Baum, R. Bernard, and H. Shechter, *ibid.*, **89**, 5307 (1967).

(12) G. L. Closs and L. E. Closs, *ibid.*, **83**, 1003 (1961).

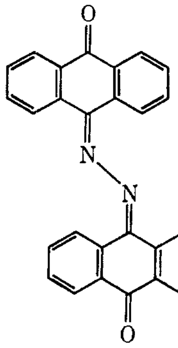
(13) L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).

(14) R. Huisgen and R. Knorr, *Naturwiss.*, **48**, 716 (1961), and W. Ried and M. Schön, *Ann. Chem.*, **689**, 141 (1965), have reported addition of diazo compounds to benzyne.

(15) (a) Diazomethane reacts with 9,10-phenanthrenequinone to give the ketoepoxide and the diepoxide.[15b] Homologous diazoalkanes and the quinone give dioxoles,[15c,d] however. (b) B. Eistert, G. Fink, and R. Wollheim, *Ber.*, **91**, 2710 (1958). (c) N. Latif and I. Fathy, *Can. J. Chem.*, **37**, 863 (1959). (d) A. Schönberg and G. Schütz, *Ber.*, **95**, 2386 (1962).

for carbonyl groups at 6.00 (benzoyl) and 6.14 μ (dienone) and its nmr signals for singlets of proper area for methyl, cyclopropyl, and vinyl hydrogens at τ 8.07, 5.56, and 3.29, respectively. The benzoyl groups in **29** are assumed to be *trans*.[16]

Thermolysis of **1** in refluxing benzene is greatly accelerated by copper and leads to the formation of 9,10-anthraquinone azine (**30**) and $\Delta^{10,10'}$-bianthrone (**26**). Azine **30** is not converted into **26** under the previous reaction conditions. Photolysis of **1** (broad spectrum) in benzene produces biphenyl (**35**, 36%) and 10,10'-bianthrone (**36**, 44%) along with **30** (2%) and 10-phenylanthrone (**37**). Possible intermediates **26** and **30** are not involved in this system since they are not converted into **36** under the photolytic conditions. Although the mechanisms of these reactions have not been established, **35** appears to be derived by photolysis of **1** into the excited diazo compound and/or the energetic carbene **31** which abstracts hydrogen from benzene (eq 6, Scheme II) to give 10-anthronyl (**32**) and phenyl (**33**) radicals.[17] Addition of **33** to benzene and subsequent hydrogen transfer (eq 7) or less probably pairing of **33** may give **35**. 10-Anthronyl radicals (**32**) apparently dimerize into **36** (eq 8). Reaction of **32** with benzene (eq 9) or less likely with **33** or by insertion of **31** into benzene may give **37**.



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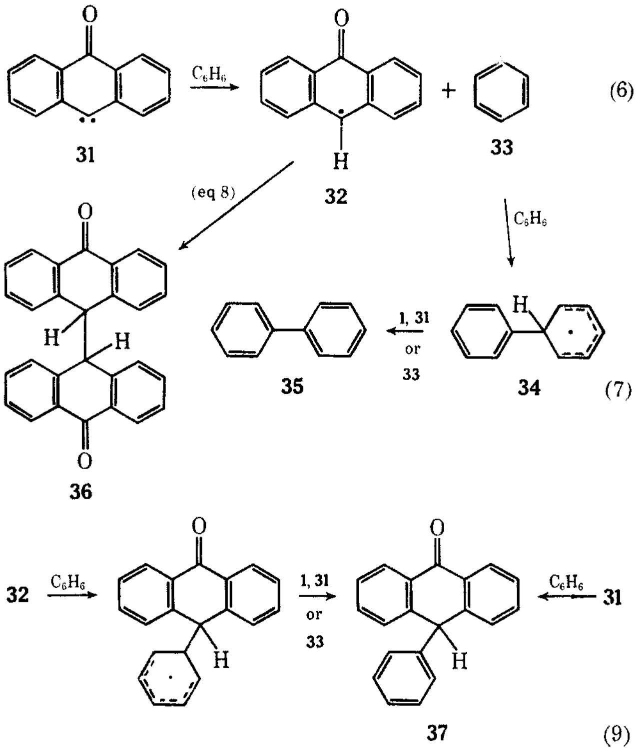
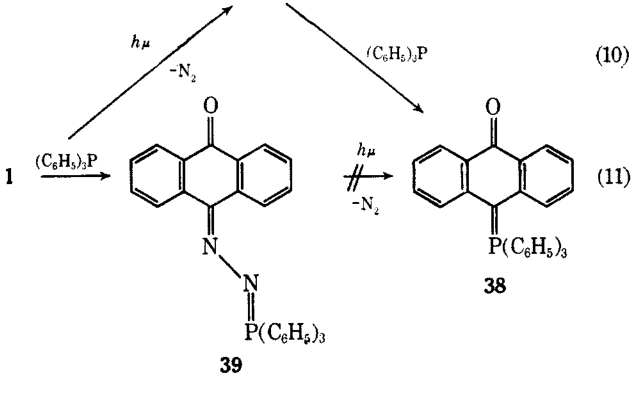
The hydrogen transfer reaction to carbene **31** as generated photochemically (eq 6) is consistent with the observation that 1% ethanol in benzene allows photolysis of **1** to **36** (47%); the yield of **35** (9%) is greatly diminished; and **30** is not formed.[18] Carbene **31** as generated thermally and, presumably, involving the triplet abstracts hydrogen as the principal product of decomposition of **1** in refluxing xylene and in mesitylene at 120° is **36**.[19] Carbene **31** may be captured however before it effects hydrogen transfer as photolysis of **1** at 25° in benzene containing triphenylphosphine yields 10-triphenylphosphoranylanthrone (**38**) (eq 10, Scheme III). At 25° triphenylphosphine reacts very slowly with **1** to give 9,10-anthraquinone monotriphenylphosphazine (**39**, eq 11); **39** is not converted into ylide **38** (eq 11) under the previous photolytic conditions.

SCHEME II



SCHEME III



Admixture of **2** and triphenylphosphine in benzene and immediate photolysis as previously with **1** results in 2-methyl-1,4-naphthoquinone 4-triphenylphosphazine (**40**). The photolytic behavior of triphenylphosphine systems containing **1** and **2** is thus quite different. The reason for this is that **2** reacts much faster than **1** with triphenylphosphine to form their phosphazines. Phosphazine **40** is stable to irradiation whereas **1** photolyzes fairly rapidly. Diazo absorption in **1** occurs at 2070 cm^{-1} whereas **2** absorbs analogously at 2090 cm^{-1}. Diazo compounds in which the wavenumbers for their diazo absorption are greater are reported to be more

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(16) (a) Spiro[2.5]octa-2,5-dien-4-ones have been obtained in low yields from diazoalkanes and methylenecyclohexadienones[16b] and from 2-*p*-hydroxyphenylethyl bromide.[16c] After the present work had been completed, spiro[2.5]octa-2,5-dien-4-ones were prepared by photolysis of 3,5-di-*t*-butylbenzene 1,4-diazooxide in olefins.[16d] (b) D. H. R. Barton and J. B. Hendrickson, *J. Chem. Soc.*, 1028 (1956). (c) R. Baird and S. Winstein, *J. Amer. Chem. Soc.*, **85**, 567 (1963), and references therein. (d) G. F. Koser and W. H. Pirkle, *J. Org. Chem.*, **32**, 1992 (1967).

(17) (a) A second example of hydrogen transfer of this type has been observed in photolysis of spiro[fluorene-9,3'-indazole] in benzene.[11f] (b) For detailed studies of reactions of phenyl radicals with benzene, see D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 3412 (1964), and references therein.

(18) It is presumed that **31** reacts with ethanol to give **32** and $CH_3\dot{C}HOH$ and the subsequent products thereof.

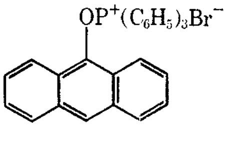
(19) (a) Thermolysis of **1** in mesitylene also yields 10,10-bis(3,5-dimethylbenzyl)anthrone. (b) G. Cauquis and G. Reverdy, *Tetrahedron Lett.*, 1493 (1967) and 1805 (1968), have also studied the photolytic behavior of **1** in various solvents and concluded that the transfer properties of **31** are derived as its triplet.

reactive in coupling with electron-donor systems.[20] The rationalization for this is based on the greater contribution of **41′** to the structure of the diazo compound (**41**) as reflected in the increased wavenumber for absorption. The greater reactivity of **2** than of **1** with triphenylphosphine is consistent with the spectral properties of the diazo compounds.

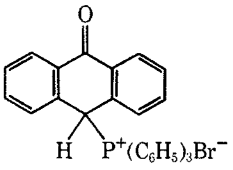
$$>C{=}N_2 \longleftrightarrow >\overset{-}{C}{-}N_2^{+}$$

41 41′

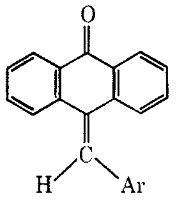
The chemistry of **38** has been investigated briefly. Attempts to synthesize **38** by standard procedures are largely unsuccessful. When **4** is mixed with triphenylphosphine in chloroform, a yellow crystalline compound which exhibits no carbonyl absorption is produced (61%). The product hydrolyzes rapidly to anthrone and triphenylphosphine oxide and is assigned the anthracene-9-oxytriphenylphosphonium bromide (**42**) structure. Precedent exists for formation of O-phosphonium bromides in related systems, and in the present case the mechanism probably involves attack of triphenylphosphine on the carbonyl group of **5** with displacement of bromine.[21] Reaction of **5** with triphenylphosphine in benzene yields a mixture of solids which exhibits weak carbonyl absorption and consists of the O- and C-phosphonium bromides (**42** and **43**). Upon reaction of the mixture with potassium *t*-butoxide in benzene, **38** is obtained in low yield.



42



43



44a, Ar = *m*-$O_2NC_6H_4$
b, Ar = *p*-$O_2NC_6H_4$

Phosphorane **38** is unreactive to refluxing acetone (10 days) and reacts only slowly with benzaldehyde. Both *m*- and *p*-nitrobenzaldehydes are converted by **38** into their 10-benzylideneanthrones (**44a** and **44b**) in high yields.

1 exhibits typical cationic behavior in acidic environments. Acetic acid converts **1** into 10-acetoxyanthrone (79%).[22] Diazo derivatives **2** and **3** are also decomposed with loss of nitrogen by various acidic reagents.

Experimental Section

10,10-Dibromoanthrone (4).[23]—A solution of bromine (44 ml, 0.86 mol) in carbon disulfide (100 ml) was added to anthrone (69 g, 0.35 mol) in carbon disulfide (1400 ml). Nitrogen was passed over the mixture to sweep out the hydrogen bromide. After several hours, the mixture was washed with saturated aqueous sodium thiosulfate. The organic layer was dried ($MgSO_4$), filtered, diluted with petroleum ether (30–60°), and refrigerated to complete crystallization. The product was washed with petroleum ether: yield, 87 g (70%); mp 148–151° dec. Recrystallization from carbon tetrachloride gave off-white rhombic prisms of **4** (63 g, 50%), mp 155–156° (dec with prior darkening), which were advantageously stored under nitrogen at 0–5°.

9,10-Anthraquinone Monohydrazone (7).—Hydrazine hydrate (35 ml, 0.70 mol) in absolute ethanol (600 ml) at 45° was added to powder-fine **4** (24.6 g, 0.07 mol). In 0.5 hr the temperature was raised to 60°, all of the **4** dissolved, and a product began to separate. After water (150 ml) had been added, the mixture was cooled to 5°. Filtration and drying gave a yellow powder (13.2 g). The product was refluxed in 95% ethanol (500 ml) and filtered; **6** (5.3 g, 32%) remained, mp 186–189° dec.[24] Crystalline **7** (6.15 g, 40%) separated from the filtrate at 4°: mp 174–175° dec. Recrystallizations from ethanol gave brown-orange needles: mp 175–176° dec; ir^{24c} C=O (6.12 μ) and C=NNH_2 (3.05, 3.17, 6.31, and 13.6 μ).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61. Found: C, 75.50; H, 4.47; N, 12.64.

9,10-Anthraquinone Mono-*p*-tosylhydrazone (8).—*p*-Toluenesulfonylhydrazide[25] (93 g, 0.50 mol) in anhydrous ethanol (1500 ml) at 38° was added to finely ground **4** (52.7 g, 0.15 mol). The mixture was stirred at 35° for 6 hr and cooled to 5°. The yellow precipitate was washed with cold absolute ethanol and vacuum dried. Crude **8** weighed 43 g (76%) and melted around 148° dec. Owing to its instability **8** was used without further treatment. Preparation of **8** in benzene gave pure product as yellow square rods in low yield: mp 149–151° dec; ir^{24c} C=O (6.10 μ).

Anal. Calcd. for $C_{21}H_{16}N_2O_3S$: C, 67.01; H, 4.28; N, 7.44. Found: C, 67.16; H, 4.07; N, 7.32.

Preparation of 10-Diazoanthrone (1). A. From 9,10-Anthraquinone Monohydrazone (7).—A solution of **7** (2.2 g, 0.01 mol) in tetrahydrofuran (40 ml) was stirred at 25–30° with yellow mercuric oxide (2.4 g, 0.011 mol) for 28 hr. Suction filtration using cellulose filter aid and removal of the solvent *in vacuo* gave crystalline **1** (2.1 g, 96%). The conversion was effected more rapidly and in 97% yield using silver oxide.

B. From 9,10-Anthraquinone Mono-*p*-tosylhydrazone (8).—Aqueous sodium hydroxide (1 *N*, 530 ml) was added to **5** (43 g, 0.114 mol) in methylene chloride (530 ml). The mixture was shaken for several min. The deeply colored organic layer was separated and the aqueous layer washed with methylene chloride. The combined methylene chloride extracts were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The resultant crystalline **1** weighed 24.9 g (98%). Recrystallization of **1** from carbon tetrachloride afforded red-brown needles which decompose before melting: ir C=N_2 (4.87) and C=O (6.11 μ).

Anal. Calcd for $C_{14}H_8N_2O$: C, 76.34; H, 3.66; N, 12.77. Found: C, 76.19; H, 3.57; N, 12.80.

C. From 9,10-Anthraquinone Monooxime (9).—A solution of the sodium salt of **9** was prepared by dissolving the parent oxime[26] (2.2 g, 0.01 mol) in aqueous sodium hydroxide (4%, 200 ml), washing with ether (100 ml), and separating the red aqueous layer. The aqueous mixture was cooled to 0°, and concentrated ammonium hydroxide (20 ml, 0.30 mol) and then aqueous sodium hypochlorite (140 ml, 5.25%, 0.10 mol) were dropped into the stirred solution. Gas was evolved. After 1 hr the precipitate (1.3 g) was collected and dried.

The ir of the product indicated that it was approximately a 50:50 mixture of **1** and **11**. Imine **11** (0.7 g) was separated by vacuum sublimation. Its infrared absorption was identical with that of an authentic sample.[27] Aqueous acetic acid converts **11** quantitatively into 9,10-anthraquinone.

2′-Cyanospiro[anthrone-10,1′-cyclopropane] (12).—A solution of **1** (2.2 g, 0.01 mol) and acrylonitrile (2 ml, 0.03 mol) in benzene (100 ml) was refluxed under nitrogen for 20 hr during which time theoretical nitrogen was evolved. After the mixture had been cooled to room temperature, concentrated *in vacuo*, and filtered, **12** crystallized from 95% ethanol as white needles (1.69, 65%). Recrystallizations from ethanol yielded a constant-melting product: mp 187–189°; ir C=C (6.07) and C≡N (4.53 μ); nmr ($DCCl_3$ was used throughout this study) cyclopropyl **H** (τ 7.62, m, 3) and aromatic **H** (1.3–3.2, m, 8).

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(21) B. Miller, *J. Org. Chem.*, **28**, 345 (1963); I. J. Borowitz and R. Virkhaus, *J. Amer. Chem. Soc.*, **85**, 2183 (1963), and references therein.

(22) Reference 5a reports the analogous behavior of **1** in formic acid.

(23) Modification of the procedure of F. Goldmann, *Ber.*, **20**, 2436 (1887).

(24) (a) K. H. Meyer and A. Sander, *Ann. Chem.*, **396**, 133 (1913). (b) Handling of **6** is complicated by its elimination of hydrogen bromide. (c) As KBr wafer.

(25) L. Friedman, R. Litle, and W. Reichle, *Org. Syn.*, **40**, 93 (1960).

(26) P. L. Julian, W. Cole, and G. Diemer, *J. Amer. Chem. Soc.*, **67**, 1721 (1945).

(27) M. L. Stein and H. von Euler, *Gazz. Chim. Ital.*, **84**, 290 (1954).

Anal. Calcd for $C_{17}H_{11}NO$: C, 83.24; H, 4.52; N, 5.71. Found: C, 83.28; H, 4.47; N, 5.58.

2′-Acetylspiro[anthrone-10,1′-cyclopropane] (13).—A mixture of 1 (2.2 g, 0.01 mol) and methyl vinyl ketone (2.1 g, 0.03 mol) in benzene (100 ml) was refluxed under nitrogen until gas evolution was complete (8 hr). Removal of solvent *in vacuo* led to a red oil which crystallized upon seeding and storing at 5°. Trituration with petroleum ether (30–60°, 25 ml) and filtration gave a product (2.5 g) which was recrystallized from cyclohexane. The pale yellow needles of **13** weighed 1.6 g (61%): mp 115–116°; ir CH_3C=O (5.91) and anthrone C=O (6.07 μ); nmr cyclopropyl **H** (τ 7.0–7.9, m, 3), CH_3C=O (8.27, s, 3), and aromatic **H** (m, 8).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.60; H, 5.51.

2′-Carbomethoxy-2′-methylspiro[anthrone-10,1′-cyclopropane] (14).—Methyl methacrylate (3 g, 0.03 mol) and 1 (2.2 g, 0.01 mol) in benzene (100 ml) under nitrogen was refluxed for 2 days during which time approximately theoretical nitrogen was evolved. Solvent removal *in vacuo* left an oil and an amorphous solid. This mixture was refluxed briefly with absolute alcohol (50 ml) and then refrigerated. After filtering the polymerlike solid, the filtrate was concentrated by vacuum evaporation. The residue crystallized from petroleum ether. The crude product was charcoaled and recrystallized from cyclohexane to give **14** (1.65 g, 56%), mp 107–110°. An analytical sample as colorless needles melted at 110–112°: ir ester C=O (5.80) and anthrone C=O (6.04 μ); nmr (CCl_4) C-methyl **H** (τ 8.98, s, 3), O-methyl **H** (6.95, s, 3), cyclopropyl **H** (q, 2, J = 7.5 cps), and aromatic **H** (2 m, 8).

Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.94; H, 5.67.

***trans*-2′,3′-Dibenzoylspiro[anthrone-10,1′-cyclopropane] (15).**—A mixture of 1 (2.2 g, 0.01 mol) and *trans*-1,2-dibenzoylethylene (2.61 g, 0.011 mol) under nitrogen in benzene (100 ml) was refluxed until evolution of nitrogen ceased (~7 hr). The vacuum concentrate was triturated with 95% ethanol (35 ml) and the slurry filtered. The off-white residue, mp 211–215° dec, weighed 3.9 g (91%). Recrystallization from benzene afforded colorless prisms of **15** (3.1 g): mp 220–222° dec; ir C=O (d, 6.0 μ); nmr cyclopropyl **H** (τ 5.61, s, 2) and aromatic **H** (2 m, 18).

Anal. Calcd for $C_{30}H_{20}O_3$: C, 84.09; H, 4.70. Found: C, 84.31; H, 4.71.

Spiro[anthrone-10,7′-bicyclo[4.1.0]hept-3′-ene-2′,5′-dione] (18) and 4′,7′-Dihydroxyspiro[anthrone-10,3′-indazole] (17). A. At 80°.—*p*-Benzoquinone (3.2 g, 0.03 mol) and 1 (2.2 g, 0.01 mol) in benzene (100 ml) was refluxed until 1 equiv of nitrogen was evolved (22 hr). The dark mixture was cooled, filtered, and concentrated *in vacuo*. The residue was boiled for a few min in absolute ethanol (25 ml), cooled, and filtered to give a product (2.2 g), which was treated with charcoal in boiling absolute ethanol (150 ml). After filtering the hot suspension and cooling, a yellow solid (1.3 g) deposited. Recrystallization from alcohol yielded yellow crystals of **18** (1.2 g, 37%): mp 168–170° dec; ir C=O (d, 6.0 μ); nmr cyclopropyl **H** (τ 6.77, s, 2), vinyl **H** (τ 3.37, s, 2), and aromatic **H** (m, 8).

Anal. Calcd for $C_{20}H_{12}O_3$: C, 79.99; H, 4.03. Found: C, 79.84; H, 4.41.

B. At 20–30°.—In a similar experiment 1 was stirred with *p*-benzoquinone at room temperature. In 3 days the benzene solution deposited an orange-yellow solid (0.7 g). The infrared spectrum of this material exhibited intense diazo absorption (4.83 μ); however, the balance of the spectrum did not indicate the presence of 1. The product was treated with hot acetonitrile (70 ml) and filtered and the filtrate cooled. Crude **17** (0.2 g, 6%) deposited. Recrystallizations from acetonitrile afforded small yellow prisms which decomposed above 140°: ir OH (3.1) and C=O (6.11 μ).

Anal. Calcd for $C_{20}H_{12}N_2O_3$: C, 73.16; H, 3.68; N, 8.53. Found: C, 73.14; H, 3.73; N, 8.64.

Work-up of the initial filtrate resulted in isolation of **18**.

N-Phenyl-9,10-anthraquinone Monoimine N-Oxide (19).—A solution of 1 (2.2 g, 0.01 mol) and nitrosobenzene (1.1 g, 0.01 mol) in benzene (100 ml) was stirred at 20–25° until 1 equiv of nitrogen was evolved (1.5 days). Removal of the solvent *in vacuo* yielded an orange-red oil which solidified upon refrigeration. Trituration with petroleum ether (30–60°) followed by filtration left an orange powder which after recrystallization from 95% ethanol gave **19** (2.15 g, 72%), mp 144–146° dec. Recrystallizations from alcohol led to purer **19**: yellow leaves; mp 150–152° dec; ir C=O (6.03 μ).

Anal. Calcd for $C_{20}H_{13}NO_2$: C, 80.25; H, 4.38; N, 4.68. Found: C, 80.01; H, 4.02; N, 4.63.

N,N-Dicarbethoxy-9,10-anthraquinone Monohydrazone (20).—Reaction of 1 (2.2 g, 0.01 mol) and diethyl azodicarboxylate (3.5 g, 0.02 mol) in benzene (100 ml) was effected at room temperature for 1 day during which time *ca.* 50 ml of nitrogen was evolved. The mixture was then refluxed for 20 hr and the theoretical quantity of nitrogen (0.01 mol) was expelled. Solvent removal *in vacuo* gave a red oil which eventually solidified at 25°. Trituration with benzene–petroleum ether and filtration gave 3.5 g of product. Recrystallization from absolute ethanol yielded yellow leaves of **20** (2.55 g, 75%), mp 148–152°. Recrystallizations from ethanol and from benzene afforded an analytical sample: mp 151–152.5°; ir urethan C=O (5.73) and anthrone C=O (5.97 μ); nmr methyl **H** (τ 8.87, t, 6), methylene **H** (5.82, q, 4), and aromatic **H** (m, 20).

Anal. Calcd for $C_{20}H_{18}N_2O_5$: C, 65.57; H, 4.95; N, 7.64. Found: C, 65.49; H, 5.10; N, 7.52.

4′,5′-Dicarbomethoxyspiro[anthrone-10,3′(3′H)-pyrazole] (21).—Diazooxide 1 (6.6 g, 0.03 mol) and dimethyl acetylenedicarboxylate (4.56 g, 0.03 mol) in benzene (250 ml) were stirred at room temperature for 5 days. The solution turned light orange but no nitrogen was evolved. Solvent removal *in vacuo* left an orange solid, mp 109–115° dec, which upon crystallization from benzene–Skellysolve C, yielded crystals (7 g, 64%) of **21**, mp 123–125° dec. An analytical sample, yellow crystals which became orange upon drying *in vacuo* at 56° for 1 hr, was obtained by further recrystallizations from benzene–Skellysolve C and ethanol, mp 124.5–125.5° dec.

Anal. Calcd for $C_{20}H_{14}N_2O_5$: C, 66.30; H, 3.89; N, 7.73. Found: C, 66.53; H, 4.00; N, 7.86.

The product crystallizes in one or both of two forms, square rods or irregular prisms. Both decompose at the same temperature but their infrared spectra in potassium bromide wafers are considerably different. However, their spectra in chloroform are identical: ester C=O (5.78) and anthrone C=O (6.01 μ); nmr O-methyl **H** (τ 5.99, s, 3, and τ 6.54, s, 3) and aromatic **H** (m, 8).

Photolysis of 4′,5′-Dicarbomethoxyspiro[anthrone-10,3′(3′H)-pyrazole] (21). 1′,2′-Dicarbomethoxyspiro[anthrone-10,3′-cyclopropene] (22).—Photolysis of 21 (3.0 g, 8.3 mmol) in anhydrous ether (300 ml) purged with nitrogen caused evolution of 1 equiv of nitrogen.[28] Solvent reduction *in vacuo* caused the crystallization of pale yellow **22** of irregular decomposition point with yield, 1.3 g, 47%. Several recrystallizations (CCl_4) afforded an analytical sample which slowly decomposed over a wide range above 125°: ir cyclopropene (5.44), ester C=O (5.83), and anthrone C=O (6.10 μ); nmr O-methyl **H** (τ 6.20, s, 6) and aromatic **H** (2m, 8).

Anal. Calcd for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.67; H, 4.22.

Spiro[anthrone-10,3′-indazole] (23).—A solution of anthranilic acid (1.44 g, 0.0105 mol) in acetone (12 ml) was added dropwise in 1.5 hr to a refluxing mixture of 1 (2.2 g, 0.01 mol) and isoamyl nitrite (1.35 g, 0.0115 mol) in dichloromethane (50 ml).[14] During addition the theoretical volume of nitrogen and carbon dioxide (450 ml, 0.02 mol) required for generation of benzyne was evolved. The red solution was then refluxed for a few minutes, cooled, and concentrated *in vacuo* at 20–30°. The oily crystalline residue was washed with 95% ethanol and filtered to yield **23** (2.60 g, 87%), mp 174° dec. Several recrystallizations from acetonitrile yielded **24** as nearly colorless prisms: mp 179–180° dec; ir C=O (6.02 μ).

Anal. Calcd for $C_{20}H_{12}N_2O$: C, 81.06; H, 4.08; N, 9.45. Found: C, 81.05; H, 3.88; N, 9.71.

Spiro[anthrone-10,2′-(phenanthro[9.10]-1′,3′-dioxole)] (24).—A benzene solution (100 ml) of 1 (2.20 g, 0.01 mol) and 9,10-phenanthrenequinone (2.08 g, 0.01 mol) was refluxed for 4.5 days while nitrogen (195 ml, 87%) was evolved. Filtration of the cooled reaction mixture separated 9,10-anthraquinone azine (**30**, 150 mg, 7.2%) as shown by its infrared spectrum.

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[28] Photolyses were effected externally with a Hanovia 450-W mercury arc lamp, type L (679 A-10). The photolysis vessel was a quartz tube (4.5 × 400 cm) fitted with a condenser. Stirring was accomplished magnetically and the temperature was maintained at or below that of the room by passing a stream of water over the photolysis tube. Evolution of nitrogen was monitored by collection over water.

The residue obtained by concentrating the filtrate was treated with charcoal in boiling acetonitrile (550 ml) and filtered. Upon cooling, **24** (1.4 g, 35%), mp 269–273°, separated. After the filtrate had been concentrated to *ca.* 200 ml, a second crop of crystals was obtained which was contaminated with $\Delta^{10,10'}$-bianthrone (**26**) as indicated by its infrared spectrum and its green fluorescence under ultraviolet light. An analytical sample of **24** was obtained as yellow needles and plates after chromatography on alumina and recrystallizations from acetonitrile: mp 271–273° dec with prior darkening; ir C=O (6.0 μ).

Anal. Calcd. for $C_{28}H_{16}O_3$: C, 83.98; H, 4.02. Found: C, 83.96; H, 3.98.

***trans*-2,3-Dibenzoyl-2'-methylspiro[cyclopropane-1,4'-(1'-[1'H,4'H]-naphthalenone)] (27).**—Approximately 1 equiv of nitrogen was evolved upon stirring a solution of **2** (1.84 g, 0.01 mol) and *trans*-1,2-dibenzoylethylene (2.37 g, 0.01 mol) in benzene (100 ml) at room temperature for 1 week. A white solid (3.3 g, 84%) was collected. Recrystallizations from benzene gave **27** as colorless prisms which crumbled to a chalky white powder upon vacuum drying at 56°: mp 216–217°; ir C=O (5.94, 6.04, and 6.09 μ); nmr methyl **H** split by vinylic **H** (τ 7.93, d, 3), nonequivalent cyclopropyl **H** (5.54, q, 2, J = 7.7 cps), vinyl **H** (3.19, unresolved, 1), and aromatic **H** (m, 14).

Anal. Calcd for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found: C, 82.49; H, 5.15.

2'-Methylspiro[indazole-3,4'-(1'[1'H,4'H]-naphthalenone)] (28).—A solution of anthranilic acid (3.55 g, 0.0259 mol) in acetone (30 ml) was added in 1 hr to a refluxing solution of **2**[2] (4.55 g, 0.0247 mol) and isoamyl nitrite (3.35 g, 0.0286 mol) in dichloromethane (90 ml).[14] After a few minutes, the red mixture was cooled, dried, filtered, and stripped of solvent *in vacuo* and the dark semicrystalline residue was refrigerated. Trituration, filtration and washing with methanol allowed isolation of a light brown powder (4.2 g).

Recrystallization from methanol and charcoal yielded **28**, mp 125–126° dec. This material was eluted with dichloromethane through basic alumina. An analytical sample as large, pale yellow prisms was obtained after recrystallizations from methanol: mp 126–127° dec; nmr methyl **H** split by vinyl **H** (τ 7.89, d, 3, J = 1.4 cps), vinylic **H** (4.16, unresolved, 1), and aromatic **H** (3 m, 8).

Anal. Calcd for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.61; N, 10.76. Found: C, 78.48: H, 4.69; N, 10.89.

3,5-Dimethyl-*trans*-7,8-dibenzoylspiro[2.5]octa-2,5-dien-4-one (29).—Diazooxide **3** (1.0 g, 6.8 mmol) and *trans*-1,2-dibenzoylethylene (1.66 g, 7.0 mol) in benzene (100 ml) were stirred in darkness for 4 weeks and then refluxed for 2 hr. The residue after solvent removal *in vacuo* was recrystallized from absolute ethanol to yield crude **30** (1.05 g, 43%), mp 149–156°. Recrystallizations from ethanol and benzene gave **30** as colorless plates: mp 165–167°; ir benzoyl C=O (6.0) and dienone C=O (6.14 μ); nmr methyl **H** (τ 8.07, s, 6), cyclopropyl **H** (5.56, s, 2), vinyl **H** (3.29, unresolved, 2), and aromatic **H** (m, 10).

Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.63; H, 5.74.

Copper-Catalyzed Decomposition of 1 in Benzene.—A stirred solution of **1** (2.2 g, 0.01 mol) in benzene (100 ml) under nitrogen was refluxed over copper powder[29] (0.5 g). Nitrogen, collected over water, ceased evolving after 1 day. After 2 days the hot mixture was filtered. An orange powder (1.45 g) was separated which on the basis of its infrared spectrum was a mixture of copper (0.5 g) and 9,10-anthraquinone azine (**30**, 0.95 g, 46%).

The filtrate upon cooling crystallized as **26** (0.60 g); additional **26** (0.15 g) was isolated by concentrating the filtrate and washing the residue with acetone. The total yield of **26** was 39%, and its structure was confirmed by comparison of its melting point and ir spectrum with those of an authentic sample.[30]

Azine **30** was characterized independently. It occurred as a side product in reaction of **4** with 3 equiv of hydrazine in ethanol. Small orange needles melting above 315° were obtained by recrystallization from xylene.

Anal. Calcd for $C_{28}H_{16}N_2O_2$: C, 81.51; H, 3.91; N, 6.79. Found: C, 81.85; H, 4.29; N, 6.64.

No reaction occurred upon refluxing **30** for 30 hr in the presence of copper powder.

Photolysis of 10-Diazoanthrone (1). A. In Benzene.—A solution of **1** (1.80 g, 8.2 mmol) in freshly distilled benzene (150 ml, from calcium hydride) was irradiated under nitrogen at 29°. After 4.5 hr, evolution of gas ceased (137 ml, 0.75 equiv of nitrogen). Filtration of the suspension yielded 9,10-anthraquinone azine (**30**, 30 mg, 2%).

The orange filtrate, after concentration to *ca.* 30 ml and filtration, gave crystalline 10,10'-bianthrone (**36**, 0.690 g, 44%). The latter was characterized by an undepressed mixture melting point and spectral comparison with an authentic sample.[31]

The solvent was removed from the filtrate and the sticky solid residue was extracted with hot petroleum ether (30–60°). The gummy residue was removed by hand and solidified upon drying in vacuum (650 mg). The petroleum ether extracts were evaporated *in vacuo;* the residue (600 mg) was chromatographed on neutral alumina (Woelm I) using benzene as eluent. The foreband yielded crystalline biphenyl (**35**, 220 mg, 36% based on every molecule of **1** giving a phenyl radical), the infrared spectrum of which was identical with that of an authentic sample. Further elution with ether gave a fraction which yielded a few milligrams of crude solid whose infrared spectrum was identical with that of a similarly chromatographed sample[32] of 10-phenylanthrone (**37**).

Careful chromatography on neutral alumina (Woelm I) of the residue left from the petroleum ether extraction gave a 530 mg recovery in 12 fractions. Small amounts of **35** and **37** along with 9,10-anthraquinone (150 mg) were identified in these fractions.

To check the possibility that $\Delta^{10,10'}$-bianthrone (**26**) served as an intermediate in this reaction, it was irradiated in suspension (0.85 g in 300 ml of benzene) under the above photolysis conditions. After 4 hr the suspension was filtered free of an uncharacterized solid (0.25 g) whose infrared spectrum showed the absence of **36**. Removal of solvent from the filtrate left solid **26**.

B. In Ethanol–Benzene.—This experiment was run as above except that absolute ethanol (3.5 ml, 1%) was added. The photolysis was complete in 2 hr, at which point 220 ml (120% of theoretical nitrogen) of gas had evolved. There was no 9,10-anthraquinone azine (**30**) detectable; **26** was isolated in 47% yield, but only an 8.5% yield of **35** was obtained.

The residue after petroleum ether extraction weighed 650 mg and its infrared spectrum was essentially identical with that of the residue from the previous experiment.

Thermolysis of 10-Diazoanthrone (1) in Mesitylene.—Thermolysis of **1** (2.2 g, 0.01 mol) was effected in mesitylene (100 ml, freshly distilled) under nitrogen for 8 hr at 125°. Concentration of the orange solution and filtration enabled isolation of crystalline 10,10'-bianthrone (**36**, 0.58 g, 30%).

Solvent removal from the filtrate gave a viscous brown residue which was chromatographed on neutral alumina (Woelm I, 2 × 13 cm) with benzene. The leading edge of the dark band was collected (50 ml) and evaporated. The oily crystalline residue was triturated with Skellysolve F, filtered, and dried to yield 10,10-bis(3,5-dimethylbenzyl)anthrone (0.21 g, 4.9%): colorless needles; mp 212–214°; nmr methyl **H** (τ 8.15, s, 12), methylene **H** (6.42, s, 4), benzyl **H** C-2 (4.08, unresolved, 4), benzyl **H** C-4 (3.51, unresolved, 2), and aromatic **H** (1.7–2.9, m, 8); mass spectrum, $C_{32}H_{30}O$, 430.2297, found 430.2294.

Anal. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02. Found: C, 88.71; H, 7.00.

The remaining products were not identified since the principal objective of the experiment had been met.

Photolysis of 10-Diazoanthrone (1) and Triphenylphosphine in Benzene.—A freshly prepared solution of **1** (3.30 g, 0.015 mol) and triphenylphosphine (4.20 g, 0.016 mol) in benzene (300 ml) was photolyzed at 13°. After 7 hr, a product had collected on the walls of the photolysis tube inhibiting light passage. 10-Triphenylphosphoranylanthrone (**38**, 3.2 g) was removed by filtration and the filtrate returned to the cleaned tube for further irradiation. Additional crops brought the total yield of **38** to 5.7 g (84%). Recrystallizations from absolute ethanol gave **38** as orange needles: mp 211–214° dec; ir C=O (6.40 μ).

Anal. Calcd for $C_{32}H_{23}OP$: C, 84.56; H, 5.10. Found: C, 84.39; H, 5.07.

A suspension of 9,10-anthraquinone 10-triphenylphosphazine (**39**, 2 g, 4.1 mol) in benzene (300 ml) was similarly photolyzed. After 7 hr approximately one-half of the initial **39** was recovered; no **38** was detected.

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[29] "44F Venus, natural copper fine," U. S. Bronze Powder Works, Inc., Flemington, N. J.

[30] A. Schönberg and A. F. A. Ismail, *J. Chem. Soc.*, 307 (1944).

[31] O. Dimroth, *Ber.*, **34**, 219 (1901).

[32] E. Barnett and J. W. Cook, *J. Chem. Soc.*, **123**, 2636 (1923).

Reaction of 10-Diazoanthrone (1) and Triphenylphosphine.—Storage of 1 (2.2 g, 0.01 mol) and triphenylphosphine (5.2 g, 0.02 mol) in benzene (250 ml) in the dark for 3 weeks gave red prisms of 9,10-anthraquinone 10-triphenylphosphine (**39**, 3.2 g, 67%). Recrystallization from toluene afforded a sample melting with decomposition at 169–171°: ir C=O (6.15 μ).

Anal. Calcd for $C_{32}H_{23}N_2OP$: C, 79.65; H, 4.80; N, 5.81. Found: C, 79.88; H, 4.99; N, 5.64.

Thermolysis of 9,10-Anthraquinone 10-Triphenylphosphazine (39).—A suspension of **39** (3.1 g, 6.4 mmol) in benzene (100 ml) was refluxed for 2 days. Cooling and filtering the suspension allowed isolation of 9,10-anthraquinone azine (**30**, 0.5 g, 37%).

Removal of the solvent *in vacuo* from the filtrate and extraction of the residue with petroleum ether (30–60°) left a dark solid (1.4 g) shown by its infrared spectrum to be a mixture of **1** and **39**. After the ether extract had been treated with charcoal and the solvent removed *in vacuo*, triphenylphosphine (0.8 g, 48%) remained.

Photolysis of 3-Methylnaphthalene 1,4-Diazooxide (2) in the Presence of Triphenylphosphine.—Triphenylphosphine (2.62 g, 0.01 mol) was added to **2** (1.84 g, 0.01 mol) in benzene (300 ml). The red solution was purged with dry nitrogen for 20 min. The orange solution was photolyzed for 9 hr; only a small amount (30 ml) of nitrogen was evolved. Solvent removal *in vacuo* left a dark material (2.73 g, 81%) showing no diazo absorption. Recrystallizations from absolute ethanol gave 2-methyl-1,4-naphthoquinone 4-triphenylphosphazine (**40**) as large orange prisms, mp 165–166° dec.

Anal. Calcd for $C_{29}H_{23}N_2OP$: C, 78.01; H, 5.19; N, 6.27. Found: C, 78.04; H, 5.30; N, 6.50.

Reaction of 10-Bromoanthrone (5) with Triphenylphosphine. A. In Chloroform.—In a system protected from moisture, triphenylphosphine (5.24 g, 0.02 mol) in ethanol-free chloroform (50 ml) was added to **5** (5.46 g, 0.02 mol) in chloroform (80 ml). The mixture warmed during the addition but no precipitation occurred. Upon continued stirring the yellow solution separated a solid (*ca.* 0.5 g). The solid quickly decomposed with fuming upon exposure to the atmosphere. Solvated anthracene-9-oxytriphenylphosphonium bromide (**42**, 9.5 g, 61%) separated from the cold filtrate as large yellow prisms. The crystals tarnished in air but could be washed clean with alcohol-free chloroform. The crude sample could not be recrystallized and was analyzed directly: mp 208–210°; ir CCl_3 (13.6 μ).

Anal. Calcd for $C_{32}H_{24}BrOP \cdot 2CHCl_3$: C, 52.74; H, 3.39. Found: C, 54.96; H, 3.33.

A sample (4 g) of **42** hydrolyzed in aqueous ethanol (40 ml) at 30° to anthrone and triphenylphosphine oxide in 95 and 85% yields respectively.

B. In Benzene.—Triphenylphosphine (5.24 g, 0.02 mol) in benzene (70 ml) was added to **5**[33] (5.46 g, 0.02 mol) in benzene (200 ml). A precipitate began to form. Stirring the solution for 1 hr after the addition was complete and then filtering allowed isolation of a pale yellow solid (5.6 g). Weak carbonyl absorption at 6.00 μ indicated that the material was a mixture of the C- and O-phosphonium bromides (**42** and **43**) with the latter predominating.

The above mixture was stirred with 1 equiv of potassium *t*-butoxide (0.01 mol) in benzene (200 ml) for 4 hr and filtered. The orange filtrate yielded a solid (4.4 g) upon removal of the solvent *in vacuo*. Solvent manipulation led to crystalline 10-triphenylphosphoranylanthrone (**38**, 0.13 g).

Reactions of 10-Triphenylphosphoranylanthrone (38). A. With p-Nitrobenzaldehyde.—A solution of **38** (1.00 g, 2.18 mmol) and 1 equiv (0.33 g) of *p*-nitrobenzaldehyde in chloroform (50 ml) was refluxed for 78 hr. Solvent removal *in vacuo* left a dark oil from which triphenylphosphine oxide was separated by treatment with hot 95% ethanol (10 ml). The alcohol precipitated yellow 10-(*p*-nitrobenzylidene)anthrone (**44b**, 0.60 g, 84%) which, upon recrystallization from absolute alcohol, melted at 182–184°: ir C=O (6.03) and NO_2 (6.65 and 7.50 μ).

Anal. Calcd for $C_{21}H_{13}NO_3$: C, 77.05; H, 4.00; N, 4.28. Found: C, 76.82; H, 4.10; N, 4.27.

The crystals fluoresced yellow under ultraviolet light but showed no thermochromism upon refluxing in xylene, pressing in potassium bromide, or fusion in a sealed capillary under nitrogen.

B. With *m*-Nitrobenzaldehyde.—Using the same procedure as above, *m*-nitrobenzaldehyde reacted with **38** to give yellow prisms of 10-(*m*-nitrobenzylidene)anthrone (**44a**, 77%), mp 173–175° after recrystallization from acetic acid, lit.[34] mp 174.5 175.5°. The crystals fluoresced green under ultraviolet light but did not exhibit thermochromism.

Reaction of 10-Diazoanthrone (1) with Acetic Acid.—A solution of **1** (2.2 g, 0.01 mol) in glacial acetic acid (100 ml) was heated at *ca.* 90° for 5 hr. The mixture progressed from dark red to light orange and the theoretical volume of nitrogen (224 ml) was evolved. After the cooled solution had been filtered, the filtrate was diluted with water. 10-Acetoxyanthrone (2.0 g, 79%) was collected, mp 107–109°, lit. 108°.[35]

Registry No.—**1**, 1705-82-4; **4**, 21555-13-5; **7**, 3166-13-0; **8**, 21555-15-7; **12**, 21555-16-8; **13**, 21555-17-9; **14**, 21555-18-0; **15**, 21543-47-5; **17**, 21555-19-1; **18**, 21555-20-4; **19**, 21555-21-5; **20**, 21555-22-6; **21**, 21555-23-7; **22**, 21557-85-7; **23**, 21620-42-8; **24**, 21557-86-8; **26**, 434-85-5; **27**, 21543-48-6; **28**, 21557-87-9; **29**, 21543-86-2; **30**, 1705-81-3; **38**, 4756-26-7; **39**, 1705-80-2; **40**, 21558-17-8; **42**, 21558-18-9; **44b**, 21558-19-0; 10,10-bis(3,5-dimethylbenzyl)anthrone, 21558-20-3.

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