and 100 mg. of manganous acetylacetonate was stirred at room temperature over a period of 3 days. After removal of the solvent at reduced pressure an oily residue was obtained. It dissolved in water with soapy foams upon shaking. Isolation of pure alkylsulfonic acid was tedious and the free acid is extremely hygroscopic. Quantitative isolation was carried out by acidifying the aqueous solution of sodium alkylsulfonate and precipitating the sulfonic acid as its lead salt with lead acetate, 30% yield.

Anal. Calcd. for $C_{16}H_{34}O_6PbS_2$: C, 33; H, 5.7; S, 10.8. Found: C, 32.8; H, 6.1; S, 11.

The infrared spectrum showed absorptions at 3.0 (w), 3.4, 3.48, 3.5 (s), 6.3 (w), 6.9 (s), 7.05 (m), 7.1 (s), 8.3 (s), 9.25 (s), and 11.0 (s–b) μ.

Addition of Thiophenol to 1-Hexene.—The mixture of 17 g. (0.2 mole) of 1-hexene and 4.4 g. (0.4 mole) of thiophenol with 100 mg. each of benzoyl peroxide and manganous acetylacetonate was stirred overnight. The reaction mixture was treated with 25 ml. of ether and 10 ml. of 10% sodium hydroxide. The aqueous layer was further extracted with ether. The ether extracts furnished 2.2 g. (30%) of *n*-hexyl phenyl thioether, b.p. 265–270°.

Anal. Calcd. for $C_{12}H_{18}S$: C, 74.16; H, 9.34; S, 16.49. Found: C, 74.21; H, 9.13; S, 16.78.

Addition of Ethyl α-Bromoacetate to 1-Octene.—The mixture of 22.4 g (0.2 mole) of 1-octene and 6.7 g. (0.04 mole) of ethyl α-bromoacetate with 0.1 g. of each of benzoyl peroxide and manganous acetylacetonate was stirred at room temperature over the weekend. The solid material was filtered and the filtrate afforded 2.5 g. (22%) of the desired product, ethyl 4-bromo-1-decanoate, boiling at 125–130° (15 mm.), lit.[21] b.p. 140° (20 mm.).

Attempts to add formamide, acetic acid, and methanol to such olefins failed.

In the blank runs, the experiments were carried out in the same manner except no oxidation–reduction couple was used.

(21) R. Fittig and A. Schneegans, *Ann.*, **227**, 92 (1885).

The Reaction of 2,3-Dichloronaphthoquinone with Nucleophiles. II. Reaction with Ethyl Acetoacetate

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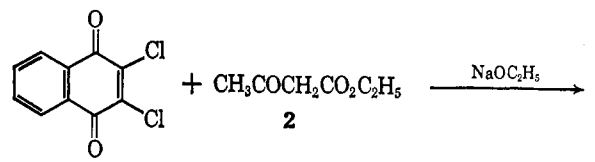
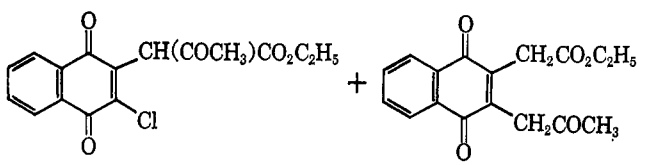
Received May 24, 1965

The course of the reaction of 2,3-dichloro-1,4-naphthoquinone and ethyl acetoacetate under basic conditions was investigated, and the structures of the products were demonstrated. A satisfactory synthesis for two of these products, **5** and **15**, is described.

In continuation of our investigation of some reactions of 2,3-dichloro-1,4-naphthoquinone (**1**) with nucleophilic reagents,[1] we examined the reaction of **1** with ethyl acetoacetate (**2**) in the presence of basic reagents. This reaction was first reported by Michel[2] who found that the addition of the sodium salt of **2** to a suspension of **1** in ethanol gave the yellow ethyl 3-chloro-1,4-naphthoquinone-2-acetoacetate (**3**) and a red by-product (A) to which he assigned the structure **4** on the basis of elementary analysis and molecular weight (301), determined by the ebullioscopic method using benzene as the solvent. This preparative method has been modified slightly[3] by adding **1** to a boiling alcoholic solution of the active methylene compound and

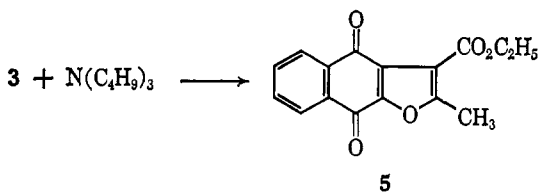


1



3 **4**

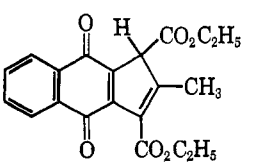
sodium ethoxide. According to Pratt and Rice,[4] the latter procedure proved to be superior for the preparation of **3**. They[4] showed that **3** was cyclized to a



5

furan derivative **5** on treatment with bases such as tributylamine. Pratt, *et al.*, reported[5] that A was obtained from reaction of **2** with 2-bromo-1,4-naphthoquinone, 1,4-naphthoquinone, or potassium 1,4-naphthoquinone-2-sulfonate under basic conditions. Pratt found it interesting that, during the formation of A, which he also formulated as structure **4**, one of the added ethyl acetoacetate moieties lost an acetyl group while the other lost a carbethoxyl group.

At about the same time of Pratt's[5] work, Suryanarayana and Telak[3] proposed a new structure for A. These authors objected to the assignment of structure **4** mainly on the basis of the red color of the material, reasoning that a compound of this structure should be yellow. They proposed structure **6** for A. Although **6** has a different molecular weight from **4**, the elemen-



6

tary compositions of both are similar. An attempt to determine the molecular weight by Rast's camphor method was not successful because of the deep color.

(1) Part I: G. A. Reynolds and J. A. VanAllen, *J. Org. Chem.*, **29**, 3591 (1964).

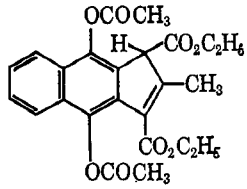
(2) F. Michel, *Ber.*, **33**, 2402 (1900).

(3) B. Suryanarayana and B. D. Telak, *Proc. Indian Acad. Sci.*, **38**, 384 (1953).

(4) E. F. Pratt and R. G. Rice, *J. Am. Chem. Soc.*, **79**, 5489 (1957).

(5) E. F. Pratt, R. W. Luckenbough, and R. L. Erickson, *J. Org. Chem.*, **19**, 176 (1954).

However, reductive acetylation of A was reported to yield a colorless diacetyl compound **7** which had the expected molecular weight. The authors concluded that the molecular weight obtained by Michel for A was in error.



7

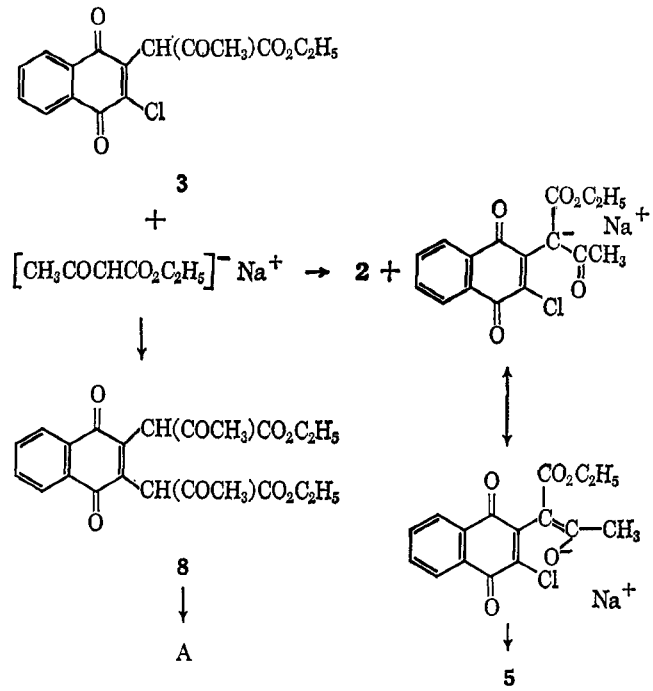
It was the purpose of our work to investigate the reactions of **1** and **2** under a variety of conditions in order to devise a method for obtaining A in good yield and also to see if evidence for structure **6** could be supplied by modern physical methods. The published procedures for the preparation of A[2,3,5] gave poor yields of A, and, on repeating this work, we found that quite a bit of material was not accounted for on the basis of isolated products. It was also found that sodium or potassium acetate was a suitable replacement for alcoholic sodium ethoxide in this reaction. Several detailed analyses were made of the reaction products obtained under different conditions to see if this would provide some explanation for the low yield of A. For example, the yields of reaction products obtained by refluxing a mixture of equivalent amounts of **1**, **2**, and potassium acetate in ethanol for 1.5 hr. were determined by means of fractional recrystallization and v.p.c. and found to be as follows: **3**, 67%; **5**, 9%; 2-chloro-3-ethoxy-1,4-naphthoquinone,[6] 8%; and **1**, 12%. The isolated yields of products obtained by several procedures are summarized in Table I.

TABLE I

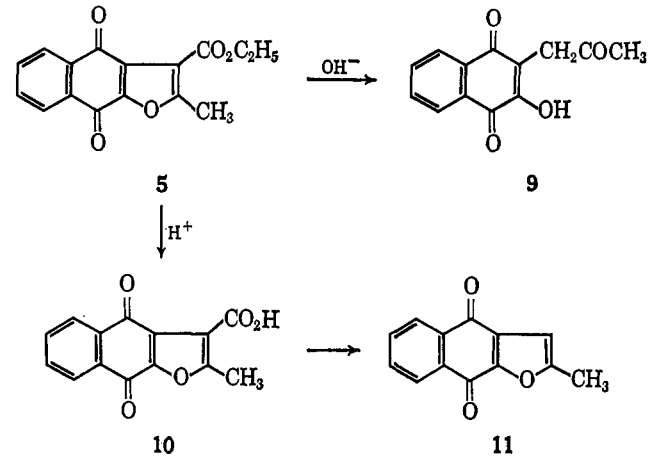
Equiv. of reactants 1	2	Base (equiv.)	Products,[a] % yield 3	A	5	Reflux time
1	2	C_2H_5ONa (2)			50	10 min
1	2	C_2H_5ONa (2)			50	5 hr.
1	1.1	C_2H_5ONa (1.1)	50	6		2 hr.
1	1	CH_3CO_2K (1)	69	3		1.5 hr.
1	1	CH_3CO_2Na (1)	68	4		1.5 hr.
1	2	CH_3CO_2Na (2)	12[b]	14	40[b]	2 hr.
1	2	CH_3CO_2Na (3)	15[b]	12	37[b]	2 hr.
1	1	$C_2H_5N[CH(CH_3)_2]_2$ (1)	85			2 hr.
1	2	$C_2H_5[CH(CH_3)_2]_2$ (2)		37[c]		

[a] Except where noted, the yields are based on isolated material. There were undoubtedly other materials present in the filtrates. [b] These yields were determined on a crude mixture by means of v.p.c. [c] Quite a bit of **3** was formed, but the product was not isolated from the filtrates.

It is evident from these results that the low yields of A were due to the competing cyclization of the intermediate monoadduct **3** to give the furan **5** in the presence of base. This behavior is due to the strongly acidic proton of **3**, and the probable reaction course is as follows. The cyclization of **3** to give **5** was investigated with various basic agents to shed some light on this competing reaction. Pratt had previously shown[4] that tributylamine effected this cyclization in 43%



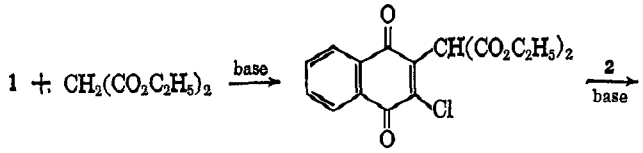
yield. We employed other bases to cyclize **3** and obtained the following yields of **5**: 42% with sodium ethoxide; 18% with potassium *t*-butoxide; and, surprisingly, 95% with piperidine. The furan **5** had been subjected to basic hydrolysis and shown to yield **9**.[4] We have hydrolyzed **5** under acidic conditions to yield **10** which was decarboxylated by means of copper chromite in quinoline to give the known compound **11**.[7]



Once it was established that the low yields of A were due to the cyclization of **3**, a new synthesis of A was devised which eliminated this possibility, and, as expected, the yield of A was greatly improved. This synthesis was based on the observation that the product **12** derived from **1** and diethyl malonate was not cyclized on treatment with base, and therefore **12** should react with **2** under basic conditions to give only one product (**13**) which could then be cyclized to give A. The synthesis is illustrated by the scheme shown. The reaction was run in alcohol solution using either sodium ethoxide or sodium acetate as the base. The intermediates **12** and **13** were isolated during several runs and then subjected to further reaction, but the

(6) L. F. Fieser and R. H. Brown, *J. Am. Chem. Soc.*, **71**, 3609 (1949).

(7) S. C. Hooker and A. Steyermark, *ibid.*, **58**, 1202 (1936).



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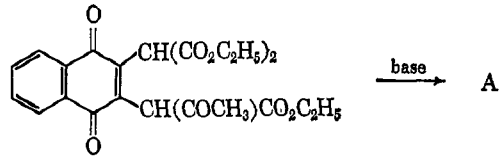

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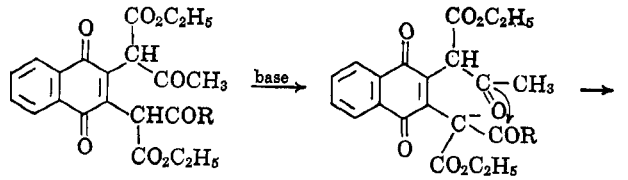
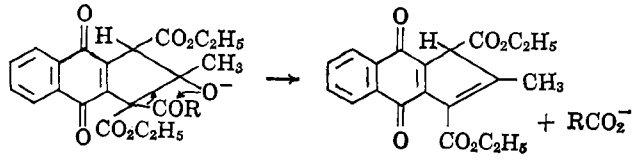
preferred method does not involve the isolation of these materials.

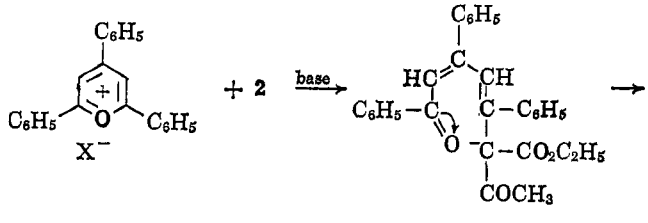
A probable reaction mechanism for the formation of **6**, assuming the obvious alkylation reactions to form **8** or **13**, is illustrated below. A similar mechanism was

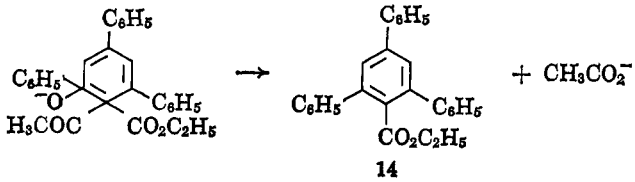


8, R = CH_3
13, R = OC_2H_5



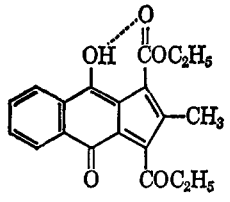
proposed[8] for the formation of **14** and is shown.





14

Compound A was subjected to analyses by a variety of physical methods and structure **15** was assigned on the basis of the results. The evidence that led to this assignment will now be discussed.[9]



15

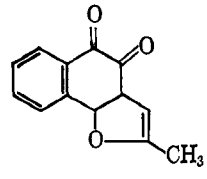
(8) K. Dimroth and G. Neubauer, *Angew. Chem.*, **69**, 720 (1957).

Mass Spectra.—Attempts to obtain the parent molecule ion of A were unsuccessful because, in spite of the relatively low melting point (152°), the compound could not be vaporized in the heated inlet of the mass spectrometer. Conversion of A to the diacetate by the published procedure[3] gave a volatile material which showed a parent molecule ion *m/e* 440, corresponding to the assigned structure **7**. In addition, there were two peaks 42 and 84 mass units below the parent peak, which is characteristic of aromatic diacetyl substituted compounds. Also, fragmentation intervals of 46 appear which can be assigned to the loss of ethanol from an ester *ortho* to a methyl group.

Molecular Weight Determination.—The average of four molecular weight determinations of A by vapor pressure osmometry in benzene solution was 355 (calculated for **6** or **15** is 354).

Infrared Spectra.—The infrared spectra of A were obtained in chloroform solution and in a potassium bromide pressing and no differences were detected. There was ester absorption at 5.8 μ and another carbonyl absorption at 6.1 μ. This latter absorption was at a longer wave length than the absorption of a large number of substituted 1,2- and 1,4-naphthoquinones which were examined. There was also an indication that a strongly bonded hydroxyl group was present.

Polarographic Analysis.—The reduction wave $E_{1/2}$ of A was found to be −0.34 v., which is typical of *p*-quinones, as opposed to *o*-quinones which show $E_{1/2}$ at *ca.* −0.10 v. For example, some representative $E_{1/2}$ values are 1,4-naphthoquinone, −0.30 v.; A, −0.34 v.; **11**, −0.27 v.; 1,2-naphthoquinone, −0.02 v.; and **16**, −0.10 v. Compound **16** was prepared by the method of Hooker.[7]

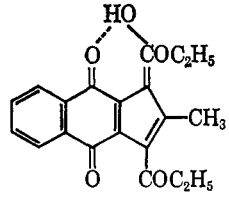


16

Nonaqueous Titration.—A nonaqueous titration of A in pyridine with 0.1 *N* tetra-*n*-butylammonium hydroxide as the titrant showed that A had approximately the same acidity as hydrochloric acid. Water-insoluble sodium and potassium salts of A were formed with weakly basic materials such as sodium cyanide and potassium acetate in alcohol solution. These salts have ultraviolet absorption spectra similar to the spectrum of the parent compound A.

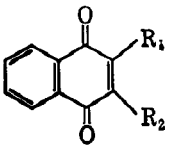
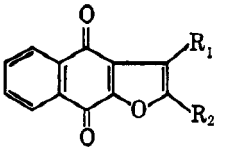
Electronic Spectra.—The ultraviolet absorption spectra of a number of 1,4-naphthoquinones which were

(9) The referee has suggested the possibility that A might have the structure



We feel that the evidence to be discussed does not allow a distinction to be made between these possibilities, but the fact that there are many examples of chelation of the enol form of a ketone with an ester group would favor structure **15**.

TABLE II
THE ULTRAVIOLET SPECTRA OF 1,4-NAPHTHOQUINONE DERIVATIVES[a]

Structure	R_1	R_2	λ, mμ (10^{-3} ε) a	b	c
					
	H	H	246 (20.4) 250 (19.8)		330 (3.0)
	H	OH	244 (16.5) 249 (18.7)	274 (16.3) 282 (15.8)	332 (3.3)
9	$-CH_2\overset{O}{\overset{\|\|}{C}}OH_3$	OH	243 (19.2) 248 (21.2)	275 (13.2)	332 (3.4)
3	$-CH(COCH_3)COOC_2H_5$	Cl	249 (24.0) 254 (30.0)	267 (19.0) ~278 (18.0)	338 (3.5)
24	$-C{=}[C(CH_3)OCOCH_3]COOC_2H_5$	Cl	247 (14.9) 253 (15.3)	275 (13.0)	338 (2.6)
					
11	H	CH_3	243 (36)	293 (6.3)	350 (2.9)
5	$-COOC_2H_5$	CH_3	250 (23)	290 (8.0)	333 (4.0)
10	-COOH	CH_3	250 (35)	301 (7.5)	345 (3.5)

[a] Acetonitrile was used as a solvent for spectral determinations.

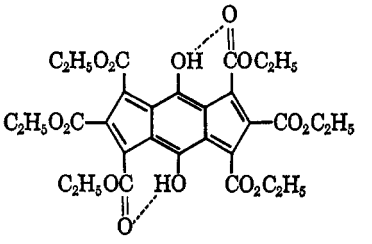
substituted in the 2- and 3-positions with various groups were examined, and they showed a consistent pattern: a high-intensity band occurred in the region of 250 mμ which was frequently split, a medium-intensity band appeared at about 275 mμ, and a low-intensity band occurred at about 335 mμ. In the case of furan derivatives such as **5**, **10**, and **11**, the latter two bands were shifted toward longer wave lengths by 10–15 mμ. The absorption data for some of the compounds of these types are summarized in Table II. There is a marked contrast between these spectra and the spectrum of compound A which had peak absorptions at 239 mμ (ε 17.3 × 10^3), 278 (2.90 × 10^3), and 460 (7.1 × 10^3). The latter band is more than 100 mμ toward the red than the absorption of typical 1,4-naphthoquinones. This shift must be related to the hydrogen bonding of a proton as represented in structure **15**, since the spectrum of **20**, in which hydrogen bonding is destroyed, has no peak at 460 mμ. The peak absorptions for 20 appear at 222 mμ (ε 20.5 × 10^3), 253 (15.4 × 10^3), and 310 (40.7 × 10^3).

N.m.r. Spectra.[10]—The data obtained from the n.m.r. spectra were most useful in the assignment of structure **15** to compound A. The data obtained from the spectra of A are tabulated in Table III and the reasons for the assignments are discussed in detail.

The most significant feature of this spectrum was the absorption at τ −6.4. The only structure that accounts for an absorption this far downfield must contain a strongly hydrogen-bonded hydroxyl group. A change in the concentration of A did not affect the position of the absorption, showing that it must be due to intramolecular hydrogen bonding, and addition of deuterium oxide caused the resonance to vanish, indicating a readily replaceable proton. The fact that the hydrogen bond must be present in a seven-membered ring was disconcerting because it was not expected that the proton resonance would be this far downfield. Recently, however, it was reported[11] that **17**, which was very similar to **15**, absorbed at τ −6.05. A Courtauld model of structure **15** showed that the hydroxyl and carbonyl groups were in an ideal position for interaction. The rigidity imposed on one of the carbethoxyl groups

TABLE III
THE N.M.R. SPECTRUM OF 15

Multiplet center (τ)	Multiplicity	Assignment
8.58	Triplet	Methyl of ethyl group
8.55	Triplet	Methyl of ethyl group
7.67	Singlet	2-Methyl
5.58	Quartet	Methylenes of ethyl group
2.44	Complex band	Phenyl protons
1.98	Complex band	Phenyl protons
−6.4	Singlet	Chelated hydroxy group



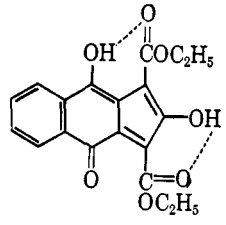
17

(10) The spectra were obtained at 60 Mc/sec. with a Varian dual-purpose V-4302 n.m.r. spectrometer equipped with a field-homogeneity control unit. The spectra were determined as 10% solutions in deuteriochloroform with 3% tetramethylsilane as an internal reference.

(11) E. LeGoff and R. B. LaCount, *Tetrahedron Letters*, No. 19, 1161 (1964).

by the chelation accounted for the two methyl triplets, since each of the ethyl groups was in a different environment, and the Courtauld model showed that the environmental differences were greater for the methyl groups than for the methylene groups. The methyl group at the 2-position had a resonance corresponding to a methyl group attached to an aromatic ring, being within a few cycles of the methyl group of toluene. Examination of the resonance bands for the aromatic protons of several 1,4-naphthoquinones, which were symmetrically and unsymmetrically substituted in the 2,3-positions, showed that the unsymmetrically substituted derivatives gave rise to two complex bands which were not mirror images of one another, whereas the symmetrically substituted derivatives gave two symmetrical complex bands arising from the AA'BB' structure. Compound A gave a pattern corresponding to an unsymmetrically substituted 1,4-naphthoquinone.

Several other compounds that were examined by n.m.r. spectroscopy for comparison with **15** also showed intramolecular hydrogen bonding. Thus the compound derived from 1 equiv. of **1** and 2 equiv. of malonic ester[12] was assigned structure **18** (hydrogen-bonded proton resonances at τ −6.64 and −0.07) and the product from **1**, malonic ester, and acetylacetone[1] was assigned structures **19a** and **19b** (hydrogen-bonded proton resonance at τ −8.75 for **19a** and τ −6.38 for **19b**).



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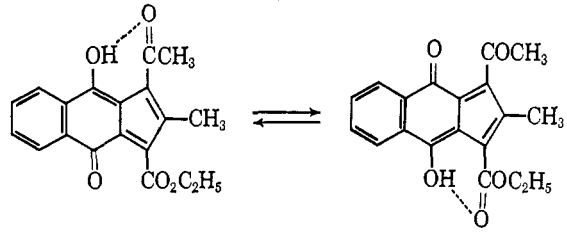
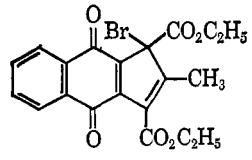


19a 19b

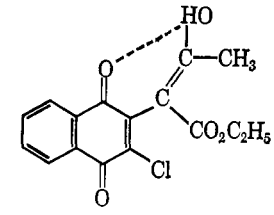
It was reported[11] that **17** was dibrominated by means of N-bromosuccinimide. In a similar manner, **15** and N-bromosuccinimide gave **20**. The n.m.r. spectra of **20** showed the following resonances in τ units: methyl of the ethyl group, 8.79 and 8.54 (triplets); methyl in the 2-position, 7.68 (singlet); methylene of the ethyl group, 5.74 and 5.55 (quartets); and phenyl protons, 2.30 and 1.90 (complex band).



20

(12) C. Liebermann, *Ber.*, **33**, 566 (1900).

The n.m.r. spectra of **3** also indicated that a hydrogen-bonded structure was present (proton resonance τ −3.18). There are several possible structures that account for this absorption, such as **21**–**23**. Although structure **23** does not contain hydrogen bonding, it was considered as a possibility. The infrared spectrum of



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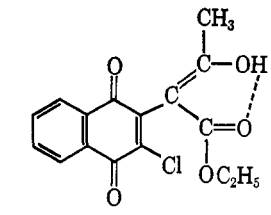

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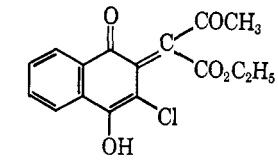
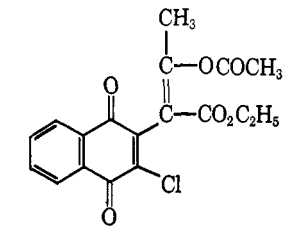


23

the compound showed that the correct structure is **22**, since there was a *p*-quinone absorption at 5.92 μ and no ester absorption at the usual wave lengths. Compound **22** was acetylated by means of isopropenyl acetate to yield a compound which was assigned structure **24** on the basis of the infrared spectrum.



24

Experimental Section

Reactions of 1 with 2.—The reactions outlined in Table I were carried out with 0.1 mole of **1** and the indicated equivalents of **2** and base with 200 ml. of absolute ethanol as the solvent. For the examples in which sodium ethoxide was the base, the appropriate amount of sodium was dissolved in alcohol, **2** was added, and the solution was stirred for 5 min.; then **1** was added and the mixture was refluxed. With other bases, the reactants were mixed and refluxed. The work-up procedure consisted of fractional recrystallizations from ethanol. Compound A was the most insoluble of the products and was readily separated. However, **3** and **5** were difficult to separate except when one was only a minor constituent, and vapor phase chromatography was the only reliable method for determining the relative amounts.

4-Carbethoxy-5-methyl-2,3-phthaloylfuran (5).—Various basic reagents were used to prepare this material as was described in the discussion. The preferred method was as follows. A mixture of 3 g. of **3**, 3 ml. of piperidine, and 30 ml. of ethanol was refluxed for 4 hr. and cooled, and the solid was collected. The solid was recrystallized from ethanol to give 2.54 g. (95%) of **5**, m.p. 163–164°.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.7; H, 4.2. Found: C, 67.5; H, 4.2.

4-Carboxy-5-methyl-2,3-phthaloylfuran (10).—A mixture of 1 g. of **5**, 10 ml. of glacial acetic acid, and 1 ml. of concentrated hydrochloric acid was refluxed for 2 hr. and cooled, and the solid was collected and recrystallized from acetonitrile to give 0.8 g. of **10**, m.p. 270°.

Anal. Calcd. for $C_{14}H_8O_5$: C, 65.7; H, 3.1. Found: C, 65.6; H, 3.3.

5-Methyl-2,3-phthaloylfuran (11).—A mixture of 3 g. of **10**, 25 ml. of quinoline, and 0.5 g. of copper chromite was refluxed for 2 hr., cooled, diluted with chloroform, and filtered, and the filtrate was extracted with dilute hydrochloric acid. The organic phase was evaporated to dryness and the residue was recrystallized from ethanol to yield 1.8 g. of **11**, m.p. 246–247°. This agrees with the reported melting point.[7]

Preparation of 15.—A solution of sodium diethyl malonate, prepared from 8 g. of malonic ester and 1.2 g. of sodium in 50 ml. of ethanol, was added to 11.3 g. of **1** dissolved in 100 ml. of dimethylformamide. The resulting solution was stirred for 3 hr. and then sodium ethyl acetoacetate, prepared from 6.5 g. of **2**, 1.2 g. of sodium, and 50 ml. of ethanol, was added. After the solution had been stirred for 2 hr., 1.2 g. of sodium and 50 ml. of ethanol were added and the mixture was heated for 0.5 hr. on the steam bath and poured into a mixture of sulfuric acid and ice. The red solid was collected and recrystallized from ethanol to give 9 g. (51%) of **15**, m.p. 152°.

Anal. Calcd. for $C_{20}H_{18}O_6$: C, 68.2; H, 5.1. Found: C, 68.2; H, 5.0.

The infrared and ultraviolet absorption curves of this material were identical with those of a sample of **15** which was prepared from **1** and **2** by the published procedure.[3]

Preparation of 13.—A solution of sodium ethyl acetoacetate from 1.3 g. of **2**, 0.23 g. of sodium, and 25 ml. of ethanol was added to a suspension of 3.5 g. of **12** in 20 ml. of ethanol, and the mixture was stirred for 2 hr. and allowed to stand overnight. The mixture was poured into cold dilute sulfuric acid; the sticky red solid was collected, washed with alcohol, and recrystallized from alcohol to give 0.6 g. of **15**. The combined alcoholic filtrates were evaporated to 10 ml. and chilled to give a yellow solid which was recrystallized from ligroin (b.p. 60–90°) to yield 1.2 g. of **13** as large yellow plates, m.p. 105°. Ultraviolet absorption in acetonitrile was as follows: 247 mμ (ε 25.3 × 10³), 253 (27 × 10³), ~260 (20.5 × 10³), and 335 (3.1 × 10³).

Anal. Calcd. for $C_{23}H_{24}O_9$: C, 62.3; H, 5.4. Found: C, 62.1; H, 5.5.

3-Bromo-3,5-dicarbethoxy-4-methyl-1,2-phthaloylcyclopentadiene (20).—A mixture of 3.5 g. (0.01 mole) of **15** and 2 g. (0.011 mole) of N-bromosuccinimide in 100 ml. of carbon tetrachloride was refluxed for 3 hr. The red color rapidly changed to pale yellow. The reaction mixture was filtered hot and the filtrate was evaporated to about 10 ml. and chilled. The yellow solid was collected and recrystallized from ligroin (b.p. 66–75°) to yield 2 g. of product, m.p. 135–136°. The product became orange on exposure to light.

Anal. Calcd. for $C_{20}H_{17}BrO_6$: C, 55.4; H, 3.9; Br, 18.4. Found: C, 55.8; H, 4.0; Br, 17.9.

3-Chloro-2-(1-carbethoxy-2-acetoxypropenyl)-1,4-naphthoquinone (24).—A mixture of 5 g. of **3**, 10 ml. of isopropenyl acetate, and 2 drops of sulfuric acid was refluxed for 1 hr. and cooled, and the solid was collected and recrystallized from alcohol to give 3.2 g. of light yellow crystals, m.p. 110°.

Anal. Calcd. for $C_{18}H_{15}ClO_6$: C, 59.5; H, 4.1; Cl, 9.8. Found: C, 59.3; H, 4.2; Cl, 9.7.

Acknowledgments.—We are grateful to G. P. Happ and D. P. Maier, for the mass spectral data; to O. E. Schupp, III, for the molecular weight determinations; to D. G. Bush, for the polarographic analysis and nonaqueous titration; and to J. K. O'Loane, for the n.m.r. spectra and their interpretation.

Synthesis of 2,2′-Bipyrroles from 2-Pyrrolinones[1a]

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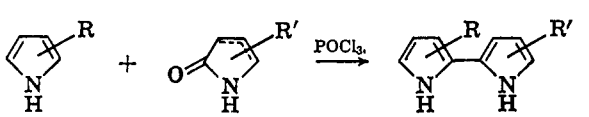
Received May 28, 1965

A series of Δ^3- and Δ^4-pyrrolin-2-ones has been prepared in which the position of the double bond has been established with certainty by reduction with diimide-d_2 and n.m.r. spectroscopy. The generalization may be drawn that Δ^3-pyrrolin-2-ones have their H-5 absorptions at lower field than the H-3 absorptions of Δ^4-pyrrolin-2-ones. Condensation of Δ^3-pyrrolin-2-ones with pyrroles leads directly in good yields to 2,2′-bipyrroles. This provides a convenient, one-step synthesis of a number of bipyrroles. However, the same reaction with Δ^4-pyrrolin-2-ones gives dipyrrylpyrrolines which may be dehydrogenated to terpyrroles. In certain instances, the presence of alkoxycarbonyl groups prevents any reaction from occurring.

The synthesis of 2,2′-bipyrroles has become of considerable interest, in part owing to the presence of such a system in the important natural products vitamin B_{12}[2] and prodigiosin.[3] Symmetrical, highly substituted 2,2′-bipyrroles are well known and are readily prepared by an Ullmann-type condensation.[4] However, unsymmetrical, simply substituted 2,2′-bipyrroles have only been prepared recently, either through the dehydrogenation of 2,2′-pyrrolidinylpyrroles (prepared from pyrroles and 1-pyrroline)[3a,5,6] or 2,2′-pyrrolinylpyrroles (synthesized from pyrroles and 2-pyrrolidinones using a Vilsmeier-type condensation).[6] Both procedures have shortcomings as general syntheses. The 1-pyrroline method suffers from both the difficulty of the initial condensation and the subsequent dehydrogenation. The Vilsmeier condensation with 2-pyrrolidinones vastly improves the condensation step, but in the case of alkylpyrroles the method is still limited by the necessary dehydrogenation step which is much improved in yield and convenience if an alkoxycarbonyl group is present somewhere in the molecule.[6b] Elimination of this troublesome dehydrogenation by employing a one-step synthesis using a 2-pyrrolinone is the next logical development in bipyrrole synthesis, and is the subject of this report.



The synthesis of 2-pyrrolinone itself has been reported[7,8] twice, the compounds obtained displaying

(1) (a) Sponsored in part by Grant AI-04888 from the National Institutes of Health, U. S. Public Health Service; (b) Public Health Service Predoctoral Research Fellow of the National Institute of General Medical Sciences.

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