TABLE I

THE AZIDES III AND THE CORRESPONDING QUINOXALINES V

| Azide, III | Yield, % | Molecular formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found | Nitrogen, % Calcd. | Nitrogen, % Found | Quinoxalines, V Yield, % | Quinoxalines, V M.p., °C. |
|---|---|---|---|---|---|---|---|---|---|---|
| a[a] | 93 | $C_8H_7N_3O$ | ... | ... | .. | .. | ... | ... | 47 | 77[b] |
| b[c] | 39 | $C_{14}H_{11}N_3O$ | 70.87 | 71.06 | 4.67 | 4.64 | 17.72 | 17.48 | 59 | 125[d] |
| c[e] | 77 | $C_9H_9N_3O$ | 61.70 | 61.60 | 5.18 | 5.34 | 23.99 | 23.35 | 47 | 64[f] |
| d[g] | 88 | $C_{10}H_{11}N_3O$ | 63.47 | 63.74 | 5.86 | 5.98 | 22.21 | 22.22 | 54 | 64[h] |
| g[i] | 84 | $C_{10}H_{11}N_3O_2$ | 58.52 | 58.24 | 5.40 | 5.30 | 20.48 | 20.72 | 40 | 244[j] |

[a] M.p. 17°. [b] O. Fischer and F. Romer, *Ber.*, **41**, 2350 (1908). [c] M.p. 85°. [d] O. Hinsberg and F. Konig, *Ber.*, **27**, 2181 (1894). [e] B.p. 75° (0.5 mm.), $n^{25}_D$ 1.5484, $d^{25}_4$ 1.1375; $MR_D$ (calcd.) 47.91, $MR_D$ (found) 48.94. [f] Lit.[11] m.p. 58°. See Experimental. [g] B.p. 74° (0.5 mm.), $n^{25}_D$ 1.5309, $d^{25}_4$ 1.0954; $MR_D$ (calcd.) 52.53, $MR_D$ (found) 53.44. [h] No depression in a mixed m.p. determination with Vc prepared from IIIc. [i] B.p. 130° (8 mm.), $n^{25}_D$ 1.5188, $d^{25}_4$ 1.1478; $MR_D$ (calcd.) 54.17, $MR_D$ (found) 54.30. [j] J. Buraczewski and L. Marchlewski, *Ber.*, **34**, 4009 (1901).

lation of benzil anil (IVe), m.p. 106–107°,[18] 19% yield from IIIe and the previously unreported anil (IVf), m.p. 170–172°, from IIIf in 14% yield.

*Anal.* Calcd. for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.28. Found: C, 80.80; H, 5.87; N, 6.10.

**Preparation of 2-Methyl-3-phenylquinoxaline (Vc).**—Following the procedure of von Auwers[11] this compound, m.p. 64–65°, was obtained in 90% yield from acetylbenzoyl[19] and *o*-phenylenediamine. In a similar reaction with α-bromopropiophenone, Vc was obtained in 87% yield. (No condensation product was detected from a mixture of isonitrosopropiophenone and *o*-phenylenediamine in refluxing ethanol.) The product was recrystallized from aqueous ethanol and from carbon tetrachloride.

*Anal.* Calcd. for $C_{15}H_{12}N_2 \cdot H_2O$: C, 75.61; H, 5.92. Found: C, 75.89; H, 5.86.

After a purified sample was dried in an Abderhalden drying pistol at room temperature, it became a viscous oil which crystallized upon standing and had a m.p. of 40–50°. (Von Auwers[11] reported a m.p. of 57–58°.) Recrystallization of the dried material from aqueous ethanol allowed recovery of the hydrate, m.p. 64–65°.

**Hydrolysis of the Anils (IVe, f).**—To a solution of 20 ml. of concentrated hydrochloric acid in 5 ml. of water was added 84 mg. (0.295 mmole) of the benzil anil (IVe). The mixture was heated on a steam-cone for 17 hours. After cooling the reaction mixture in an ice-bath, it was thoroughly extracted with ether. The combined ether extracts were evaporated in an air stream and the yellow residue recrystallized from dilute aqueous ethanol. Three recrystallizations yielded 25 mg. (40%) of cream-colored needles, m.p. 93–94°. A mixed melting point determination with an authentic sample of benzil showed no depression.

The aqueous layer from the ether extraction was made basic by adding 20% sodium hydroxide and was then extracted with ether. The combined ether extracts were evaporated in an air stream to a few drops. Ten ml. of acetic anhydride was added and the solution placed on a steam-cone 30 minutes and then evaporated to dryness in an air stream. The crystalline white residue was recrystallized as leaflets from water containing a few drops of ethanol, wt. 27 mg. (68%), m.p. 112–114°. A mixed melting point determination with an authentic sample of acetanilide showed no depression.

In a similar manner, 29 mg. (0.133 mmole) of the anil (IVf) was hydrolyzed. A solution of 0.2 g. of hydroxylamine hydrochloride and 1 ml. of 10% sodium hydroxide was added to the ether extracts. Ethanol was added until a solution was obtained, which was heated 30 minutes on a steam-cone. Upon cooling, white needles separated and were recrystallized from aqueous ethanol yielding 5.4 mg. (25%) of a monoöxime of acetylbenzoyl, m.p. 108–109°. A mixed melting point determination with an authentic sample of α-isonitrosopropiophenone (Eastman Kodak Co.) showed no depression.

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(18) F. X. Bandrowski, *Monatsh.*, **9**, 687 (1888); M. Siegfeld, *Ber.*, **25**, 2600 (1892).

(19) W. W. Hartman and L. J. Roll, *Org. Syntheses*, **23**, 1 (1943).

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

# Studies in the Wagner Rearrangement. VI. The Directive Effects of the Methyl and Methoxyl Groups[1]

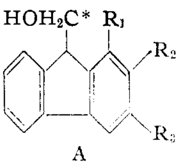
BY CLAIR J. COLLINS AND BEN M. BENJAMIN[2]

RECEIVED NOVEMBER 28, 1952

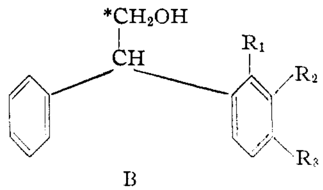
The directive effects of the 3-methyl and 3-methoxyl groups on the rearrangements of their derivatives of 9-fluorenyl (carbinol-$C^{14}$) have now been determined. The 3-methyl group enhances the ability for migration of the substituted benzo moiety in relation to the benzo-ring in the ratio 73:27. The corresponding effect of the 3-methoxyl group is to increase this ratio to 98:2. These results are compared with previous results in the 9-fluorenylcarbinol (A) and in the 2,2-diphenylethanol (B) series.

## Introduction

Previous reports[3-7] from this Laboratory have been concerned with the directive influences of various substituents on the dehydration–rearrangement reactions of carbon-14 labeled, unsymmetrically substituted 9-fluorenylcarbinols (A) and 2,2-diphenylethanols (B). We now report the results of the syntheses and rearrangements of two more



A



B

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(1) This paper is based on work performed under contract Number W-7405-eng-26 for the Atomic Energy Commission at Oak Ridge National Laboratory.

(2) That portion of this research concerned with 3-methoxy-9-fluorenyl-(carbinol-$C^{14}$) was abstracted from the Ph.D. Thesis of Ben M. Benjamin, submitted to the Graduate School of the University of Florida, Gainesville, June, 1952.

(3) C. J. Collins, J. G. Burr and B. N. Hess, THIS JOURNAL, **73**, 5176 (1951).

(4) C. J. Collins, D. N. Hess, R. H. Mayor, G. M. Toffel and A. R. Jones, *ibid.*, **75**, 397 (1953).

(5) B. M. Benjamin and C. J. Collins, *ibid.*, **75**, 402 (1953).

(6) C. J. Collins, L. S. Ciereszko and J. G. Burr, *ibid.*, **75**, 405 (1953).

(7) J. G. Burr and L. S. Ciereszko, *ibid.*, **74**, 5426 (1952).

TABLE I

DIRECTIVE INFLUENCE OF SUBSTITUENT GROUPS IN DEHYDRATION–REARRANGEMENT OF 9-FLUORENYLCARBINOLS

| Reaction No. | Substituent in A | Product | Substituted benzo group migration, % | Reference |
|---|---|---|---|---|
| 1 | $R_1 = CH_3$; $R_2 = R_3 = H$ | 1-Methylphenanthrene-9,10-$C_1^{14}$ | 50 | 5 |
| 2 | $R_1 = H$; $R_2$ and $R_3 = o\text{-}C_6H_4$ | Benzanthracene-5,6-$C_1^{14}$ | 52 | 3 |
| 3 | $R_1 = R_2 = H$; $R_3 = CH_3$ | 3-Methylphenanthrene-9,10-$C_1^{14}$ | 73 | This paper |
| 4 | $R_1$ and $R_2 = o\text{-}C_6H_4$; $R_3 = H$ | Chrysene-5,6-$C_1^{14}$ | 76 | 4 |
| 5 | $R_1 = R_2 = H$; $R_3 = CH_3O$ | 3-Methoxyphenanthrene-9,10-$C_1^{14}$ | 98 | This paper |

TABLE II

DIRECTIVE INFLUENCE OF SUBSTITUENT GROUPS IN DEHYDRATION–REARRANGEMENT OF 2,2-DIPHENYLETHANOLS

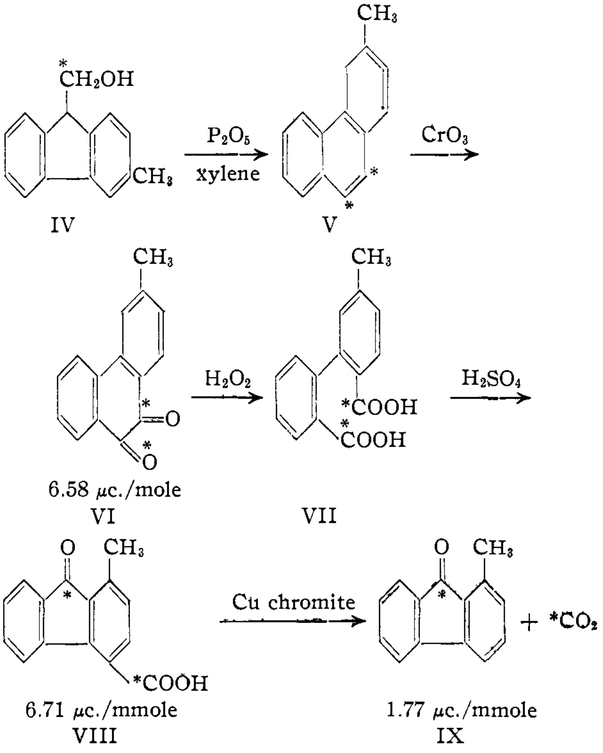
| Reaction No. | Substituent in B | Product | Subsd. phenyl-group migration, % | Reference |
|---|---|---|---|---|
| 1 | $R_1 = CH_3$; $R_2 = R_3 = H$ | 2-Methylstilbene[a] | 45 | 5 |
| 2 | $R_1$ and $R_2 = o\text{-}C_6H_4$; $R_3 = H$ | 2,3-Benzostilbene[a] | 52 | 6 |
| 3 | $R_1 = H$; $R_2$ and $R_3 = o\text{-}C_6H_4$ | 3,4-Benzostilbene[a] | 56 | 6 |
| 4 | $R_1 = R_2 = H$; $R_3 = CH_3$ | 4-Methylstilbene[a] | 66 | 7 |
| 5 | $R_1 = R_2 = H$; $R_3 = CH_3O$ | 4-Methoxystilbene[a] | 95 | 7 |

[a] Labeled in the ethylenic carbons with carbon-14.

compounds in the A series—namely, 3-methyl-9-fluorenyl-(carbinol-C$^{14}$) (IV) and 3-methoxy-9-fluorenyl-(carbinol-C$^{14}$) (XIV)—together with the degradative procedures used to locate the radioactivity distribution in their products (V and XV). The present results, as well as those described previously in this series,[3-6] are summarized in Tables I and II. Included also in Table II are two parallel results of Burr and Ciereszko.[7]

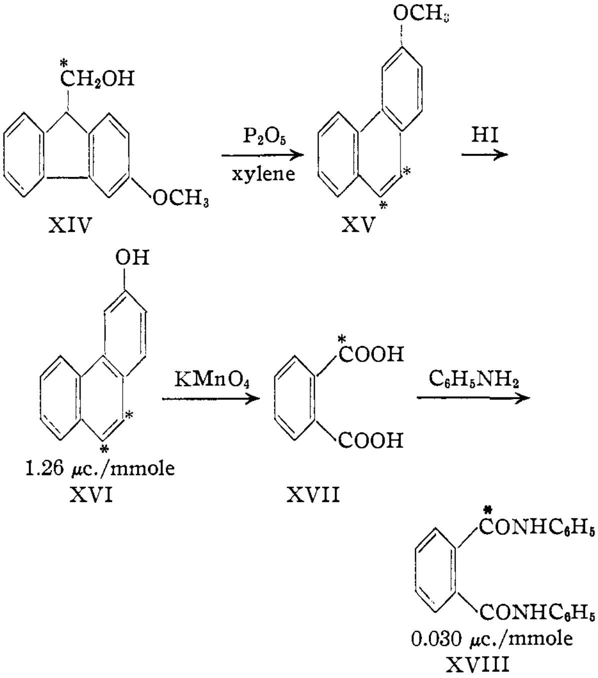
## Methods and Results

3-Methyl-9-fluorenyl-(carbinol-C$^{14}$) (IV) was prepared by methods analogous to those described in prior work.[8] The degradative procedure outlined in the reaction sequence V → IX inclusive was employed to demonstrate the amounts of carbon-14 in the 9- and 10-positions, respectively, of 3-methylphenanthrene-9,10-C$_1^{14}$ (V). It is obvious that the molar radioactivity of 1-methylfluorenone-9-C$^{14}$ (IX) represents the carbon-14 which had its origin in the 9-position of the labeled hydrocarbon (V), while the carbon atom which had its origin in the 10-position of V had been removed from the keto-acid VIII on decarboxylation. From the molar radioactivities (shown under the appropriate structural formulas) of compounds VI, VIII and IX, it may be calculated that the methyl-substituted benzo moiety of carbinol IV has migrated during the dehydration–rearrangement in preference to the unsubstituted benzo group in the ratio of 73:27.



It is noteworthy that while the dicarboxylic acid (VII) on distillation with soda lime yields 3-methyl-9-fluorenone,[9] the same compound, when treated with concentrated sulfuric acid, yields a keto-acid (VIII) which when decarboxylated produces 1-methyl-9-fluorenone (IX).

3-Methoxy-9-fluorenyl-(carbinol-C$^{14}$) (XIV) was prepared from 3-methoxyfluorene (XI) and converted to 3-methoxyphenanthrene-9,10-C$_1^{14}$ (XV) by standard methods.[3-8] The degradation represented by the sequence XV → XVIII was employed to locate the radioactivity in compound XV. From the molar radioactivities of compounds XVI (1.26 μc./mmole) and XVIII (0.030 μc./mmole) it may be shown that the 3-methoxyl-substituted benzo moiety of carbinol XIV migrated in preference to the unsubstituted benzo moiety in the ratio 98:2.



## Discussion

The electrical effects of the 3-methyl and of the 3-methoxyl groups on the dehydration–rearrangement of their 9-fluorenyl-(carbinol-C$^{14}$) (A) derivatives have now been demonstrated. Although the

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[8] C. J. Collins, THIS JOURNAL, **70**, 2418 (1948).

[9] O. Kruber, A. Max and W. Schade, *Ber.*, **71B**, 2478 (1938).

3-methyl group enhances the migrational tendency of the substituted benzo moiety over that of the unsubstituted benzo group in the ratio of 73:27, the 3-methoxyl has a much larger effect, and the corresponding ratio is 98:2. These values (reactions 3 and 5 in Table I) show a parallel correspondence with the values obtained by Burr and Ciereszko[7] (reactions 4 and 5 in Table II), demonstrating the electrical effects of the *p*-methyl (66:34) and *p*-methoxyl groups (95:5) in the 2,2-diphenyl-(ethanol-1-$C^{14}$) (B) series. These values are also, of course, in qualitative agreement with the reactivities predicted through the use of Hammett's sigma constants.[10] The differences in the corresponding ratios for the two series may obviously be attributed to the effect of the biphenylene (4a–4b) bond of the fluorene nucleus. Just how this biphenyl bond exerts its influence, however, is extremely difficult to adduce. In the rearrangement of 11H-benzo[b]-11-fluorenyl-(carbinol-$C^{14}$) (reaction number 2, Table I) the effect is to repress slightly the migration ratio of the $\beta$-naphthyl moiety (52:48), since the corresponding carbinol in the B series (reaction number 3, Table II) shows a preferential $\beta$-naphthyl group migration in the ratio 56:44. In the four other examples studied in the A series, as a comparison of Tables I and II will show, the effect of the biphenylene bond has been to increase the tendency of the substituted benzo moiety for migration. Although these differences are relatively small when ortho effects are not involved, they are far beyond the limits of error inherent in the experiments[11] and are therefore real rather than delusive in nature.

It was hoped that the migration ratios observed in the dehydration–rearrangement of carbinol IV would assist in an explanation for the results obtained in the dehydration of 1-methyl-9-fluorenyl-(carbinol-$C^{14}$) (reaction 1, Table I).[12] Since, however, the migration ratios observed both for the A and B series are probably dependent upon polar and steric requirements of the products, as well as of the carbinols from which these products are formed, it is obvious that any explanation for the apparently anomalous effects of *ortho* groups in both the A and B series can only be made on the basis of more data than are presently at hand. Such additional experiments are presently in progress.

## Experimental

**3-Methylfluorene** (I).—3-Methylphanthrene was prepared by the method of Bachmann and Cortes[13] and converted to 3-methyl-9-fluorenone.[9] Catalytic hydrogenation of this ketone by the method described previously for the preparation of 1,2-benzfluorene[3] produced the hydrocarbon (I), yield of purified 3-methylfluorene, 40%, m.p. 86–88°.[14]

**3-Methylfluorene-9-carboxylic-$C^{14}$ Acid** (II).—By a method described several times previously,[3–5,8] 278 mg. of I, 1.34 mmoles of triphenylmethylsodium in 6 cc. of ether, and 306 mg. of barium carbonate-$C^{14}$ (containing about 2 mc. of carbon-14 per millimole) were converted to 288 mg. of 3-methylfluorene-9-carboxylic-$C^{14}$ acid (II). Since the triphenylmethylsodium was the limiting reagent, the yield was 96%, m.p. 230–233° (lit.[14] gives a decomposition point of 222–225°).

**Methyl 3-Methylfluorene-9-carboxylate-$C^{14}$** (III).—A cooled solution of 30 cc. of methanol containing 1 cc. of acetyl chloride was added to a flask containing 288 mg. of II. After 20 minutes the solution was distilled under vacuum, leaving a quantitative yield (305 mg.) of the methyl ester, m.p. 81.0–81.5° after two crystallizations from hexane (performed on non-radioactive product during a previous run).

*Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.67; H, 5.89. Found: C, 80.87; H, 5.82.

**3-Methyl-9-fluorenyl-(carbinol-$C^{14}$) (IV).**—A saturated, filtered solution of $LiAlH_4$ in ether was added to the 305 mg. of III. An immediate, violent evolution of gas ensued. The mixture was treated with ethyl acetate to decompose the excess hydride then with dilute HCl. On extraction with ether and desiccation of the ether-soluble product, 311 mg. of crude carbinol (IV) was obtained (theory, 270 mg.). When crystallized once from hexane, and once from methanol-water, a previous non-radioactive sample gave a m.p. of 96–98°.

*Anal.* Calcd. for $C_{15}H_{14}O$: C, 85.70; H, 6.67. Found: C, 85.90; H, 6.65.

**3-Methylphenanthrene-9,10-$C_1^{14}$ (V).**—To the 311 mg. of crude product IV was added 197 mg. of non-radioactive carbinol (IV), 20 cc. of xylene (which had been distilled after 30 minutes reflux over $P_2O_5$) and about 200 mg. of $P_2O_5$. The mixture was boiled 30 minutes, treated with excess water, and the xylene layer plus ether washings of the aqueous layer were removed under vacuum, yielding 560 mg. of an oil. During a previous non-radioactive preparation, this oil yielded 88% of a crystalline 3-methylphenanthrene, which had a m.p. of 58–59.5° (lit.[13] 61–62°). The non-radioactive hydrocarbon, prepared by this method, was converted through 3-methylphenanthrenequinone, m.p. 202–204° (lit.[15] 205–206°) to 5-methyldiphenic acid, 201° (lit.[9] 208–209°).

**Degradation of 3-Methylphenanthrene-9,10-$C_1^{14}$** (V).—The 560 mg. of V above was dissolved in 80 cc. of ether and 1–2 cc. of this solution was added to an ether solution of 1.493 g. of non-radioactive 3-methylphenanthrene.[13] The homogeneous solution was then evaporated and desiccated. To the residue was added 75 cc. of acetic acid and 6.9 g. of $K_2Cr_2O_7$ according to the procedure of Haworth.[15] This produced 1.15 g. (66%) of crude quinone (VI), which was combined with 790 mg. of non-radioactive quinone, and crystallized twice from acetic acid; m.p. 208–210° (lit.[15] 205–206°).

*Anal.* 6.580 microcurie of carbon-14 per millimole of VI.

Following the procedure of Kruber, Marx and Schade,[9] 1.06 g. of VI was converted to 956 mg. (78%) of labeled 5-methyldiphenic acid (VII, m.p. 201–202°). This was not purified, but was dissolved immediately in 100 cc. of cold sulfuric acid, and the flask was put aside for 18 hours. The contents were then poured onto ice and the whole mixture was subjected to a continuous ether extraction. Since the yield of crude product was 1.12 g. (theory, 877 mg.), a considerable amount of sulfonation must have taken place during the ring closure. Crystallization twice from acetic acid yielded 460 mg. (53%) of pure 1-methyl-9-fluorenone-9-$C^{14}$-carboxylic-$C^{14}$ acid (VIII), m.p. 210–212°.

*Anal.* Calcd. for $C_{15}H_{10}O_3$: C, 75.62; H, 4.20. Found: C, 75.56; H, 4.37; 6.714 microcurie carbon-14 per millimole VIII.

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(10) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 188.

(11) See, for example, ref. 7 for a demonstration of the nearly negligible effect of varying solvents and dehydration catalysts on the migration ratios during the rearrangement of 2-phenyl-2-(*p*-tolyl)-ethanol-1-$C^{14}$.

(12) In ref. 3 it is pointed out that two possible explanations for the complete lack of any over-all effect by the 1-methyl group on the rearrangement of this carbinol are: (a) the steric and electrical effects of the methyl group are equal and opposite in sign, and exactly neutralize each other; (b) both the electrical and steric effects are zero. This latter explanation seems unlikely, in view of the present work—demonstrating that the methyl group of carbinol IV exerts a large directive influence during rearrangement—unless the postulate is made that methyl groups in the 1- and 3-positions of the carbinols of the A series may exhibit widely varying electrical or conjugative effects.

(13) W. E. Bachmann and G. D. Cortes, This Journal, **65**, 1332 (1943).

(14) D. Vorlander and A. Pritzche, *Ber.*, **46**, 1793 (1913), give a m.p. of 88°.

(15) R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

A solution of 434 mg. of VIII in 20 cc. of quinoline was boiled for one hour with 420 mg. of copper chromite catalyst. The solution was then filtered, poured into an ice–HCl mixture and subjected to a continuous ether extraction; yield 302 mg., IX (85%). After two crystallizations from ethanol–water the m.p. was 98–99° (lit.[16] 98–99°). Reduction of this ketone with an equal weight of 10% palladium-on-carbon catalyst in hydrogen at normal pressure produced 1-methylfluorene, m.p. 85–86° (lit.[17] 87°).

*Anal.* 1.771 ± 0.007 microcurie of carbon-14 per millimole IX.

**3-Methoxyfluorene** (XI).—3-Methoxyfluorenone, which was prepared by the procedure of Ullmann and Bleier,[18] was reduced to 3-hydroxyfluorene with red phosphorus and hydrochloric acid according to Lothrop's[19] method. 3-Hydroxyfluorene (13.5 g.) was dissolved in 40 ml. of 10% sodium hydroxide solution to which 15 g. of dimethyl sulfate was added. The reaction mixture was stirred at room temperature for three hours. The oily organic layer was extracted with ether and the ether was evaporated in a current of air. The residue of 3-methoxyfluorene was crystallized twice from ligroin; m.p. 101.0–101.5°. The yield was 13 g. (89%).

*Anal.* Calcd. for $C_{14}H_{12}O$: C, 85.7; H, 6.17. Found: C, 85.5; H, 6.33.

**3-Methoxy-9-fluorene-(carboxylic-$C^{14}$) Acid** (XII).—A 90% yield (1.21 g.) of the acid XII was obtained when 1.1 g. of 3-methoxyfluorene was treated with 28 ml. of triphenylmethylsodium solution and 0.056 mole of carbon-$C^{14}$ dioxide.[8] The acid was crystallized twice from toluene; m.p. 190.3–191.2°.

*Anal.* Calcd. for $C_{15}H_{12}O_3$: C, 75.0; H, 5.04. Found: C, 74.8; H, 5.14; 1.27 microcuries of carbon-14 per millimole of XII.

**Methyl 3-Methoxy-9-fluorene-(carboxylate-$C^{14}$) (XIII)**.—Esterification of the acid (XII) was accomplished by treating 0.718 g. of it with an excess of diazomethane in ether. A quantitative yield (0.780 g.) of the ester (XIII) was obtained. It was crystallized from ether; m.p. 108–109°.

*Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.55. Found: C, 75.5; H, 5.40.

**3-Methoxyphenanthrene-9,10-$C^{14}$ (XV)**.—To a solution of the carbinol XIV (0.652 g.) in 15 ml. of xylene was added 4 g. of phosphorus pentoxide. The mixture was heated at reflux temperature for 15 minutes. Water was added to the reaction mixture and the xylene solution was concentrated. A 93.5% yield (0.556 g.) of oily XV was isolated. It could not be caused to solidify.

**3-Hydroxyphenanthrene-9,10-$C_1^{14}$ (XVI)**.—The oily 3-methoxyphenanthrene (XV) (0.556 g.) was heated under a reflux condenser with 20 ml. of 55% hydriodic acid for two hours. The organic material was extracted with ether. The ether solution was then extracted twice with 20 ml. of 4% sodium hydroxide solution to which a trace of sodium thiosulfate had been added. Upon acidification of the basic solution, a white flocculent precipitate of XVI separated. This was extracted with ether and crystallized from light petroleum ether; m.p. 120–121° (lit.[20] 122–123°). The yield was 0.229 g. (44.2%). A mixed melting point of XVI with a sample of 3-hydroxyphenanthrene prepared by the method of May and Mosettig[21] was not depressed.

*Anal.* 1.25 microcuries of carbon-14 per millimole of XVI.

**Oxidation of 3-Hydroxyphenanthrene-9,10-$C_1^{14}$ (XVI)**.—A mixture of XVI (0.354 g.) and potassium permanganate (2.5 g.) in 40 ml. of water was heated at reflux temperature for one hour. Excess potassium permanganate was decomposed with ethanol. The manganese dioxide was separated from the aqueous solution and was washed with 10 ml. of dilute sodium hydroxide. The basic solution was acidified and extracted continuously with ether for 24 hours. After evaporating the ether, the crystalline residue remaining was washed with chloroform. Impure phthalic acid (XVII) (0.105 g.) remained. This was converted to phthalic dianilide (XVIII) and crystallized three times from ethanol; m.p. 250–251° (lit.[22] 251–252°).

*Anal.* 0.030 microcurie of carbon-14 per millimole of XVIII.

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[16] L. Chardonnens and H. Menert, *Helv. Chim. Acta*, **32**, 2340 (1949).

[17] W. C. Lothrop and P. A. Goodwin, THIS JOURNAL, **65**, 365 (1943).

[18] F. Ullmann and H. Bleier, *Ber.*, **35**, 4273 (1902).

[19] W. C. Lothrop, THIS JOURNAL, **61**, 2115 (1939).

[20] P. A. S. Smith and B. Ashby, *ibid.*, **72**, 2503 (1950).

[21] E. L. May and E. Mosettig, *J. Org. Chem.*, **11**, 12 (1946).

[22] S. Hoogewerf and W. A. Van Dorp, *Rec. trav. chim.*, **24**, 343 (1902).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# Heterocyclic Vinyl Ethers. II.[1] Benzo-1,4-dithiadiene

BY WILLIAM E. PARHAM, THOMAS M. RODER[2] AND WILLIAM R. HASEK

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The synthesis and proof of structure of benzo-1,4-dithiadiene and benzo-1,4-dithiadiene disulfone are described. The sulfur-containing ring in benzo-1,4-dithiadiene (V) has been shown to undergo electrophilic substitution reactions. The nitration of V gives a 2-nitrobenzo-1,4-dithiadiene (XI), and the reaction of V with N-methylformanilide and phosphorus oxychloride gives benzo-1,4-dithiadiene-2-carboxaldehyde (XIV). The dehydrogenation of benzo-1,4-dithiane constitutes an alternate synthetic route to the benzo-1,4-dithiadiene ring system. Other reactions related to the stability of V are reported.

In the first paper of this series,[3] it was noted that resonance interaction of the sulfur atoms may be sufficient to impart considerable stability to the 1,4-dithiadiene ring system.[4] Some evidence to support this possibility was found in the work of Levi[5] who, in 1890, reported that 1,4-dithiadiene undergoes the Friedel–Crafts reaction with acid chloride and aluminum chloride—a reaction atypical of aliphatic vinyl ethers and vinyl sulfides. We have been unable to prepare 1,4-dithiadiene by the condensation of thiodiglycolic acid and phosphorus trisulfide (Levi's procedure); therefore, we have directed our attention to other possible syntheses of the 1,4-dithiadiene ring system, so that a detailed study of the properties and reactions of compounds in this series can be made. This paper is concerned with

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[2] In part, from the Ph.D. Thesis of Thomas M. Roder, University of Minnesota, 1952.

[3] W. E. Parham, I. Gordon and J. Swalen, THIS JOURNAL, **74**, 1824 (1952). It is of interest to note that dioxadiene does not show aromatic character; therefore it can be concluded that any unusual stability of the 1,4-dithiadiene ring can be attributed to the ability of sulfur to expand its valence shell.

[4] 1,4-Dithiadiene is the isostere of cycloöctatetraene; however, unlike COT, the former may have a planar configuration.

[5] L. Levi, *Chem. News*, **62**, 216 (1890).