by Th. Wieland, Fritz and Hasspacher.[11] To a solution of 21.6 mg. of the quaternary chloride in 3 ml. of water there was added 35 mg. of sodium chlorate and one crystal of osmium tetroxide and the resulting solution was heated at 70° in a sealed tube for 90 hr. The solution was then transferred to a distilling flask and 40 mg. of periodic acid was added. The flask was then heated using a nitrogen stream for ebullition and leading the exit gases into a trap containing 2,4-dinitrophenyl hydrazine dissolved in 2 N hydrochloric acid. After the bulk of the water had been distilled, the contents of the trap were extracted with chloroform. After the chloroform extract had been dried over sodium sulfate, it was concentrated to give 11 mg. of a solid. This was filtered, then taken up in chloroform, and chromatographed over a 4:1 mixture of Bentonite and Celite. From the ethanol–chloroform eluate fractions there was isolated two crystalline dinitrophenylhydrazones. The first of these, weighing 0.9 mg. (14%), was shown to be the 2,4-dinitrophenylhydrazone of acetaldehyde by comparative paper chromatography using a heptane–methanol mixture.[17] The second fraction weighed 1.9 mg. (16%) and was identified as the 2,4-dinitrophenylhydrazone of formaldehyde by a similar comparative paper chromatogram.

Degradation of Des-C-curarine-I with Acid to Give C-Curarine-III.—A solution of 15.6 mg. of des-C-curarine-I chloride in 2 ml. of concd. hydrochloric acid was allowed to stand in the dark at room temperature for 2 days. It first became red-brown and then, eventually, yellow-brown. After removal of the hydrochloric acid *in vacuo*, the residue was taken up in water–saturated 1-butanol and chromatographed over powdered cellulose (Solka-Floc, BW-40).

By their fluoresence in ultraviolet light, six separate compounds could be detected on the column. The first of these moved with the solvent front and showed the behavior of a tertiary base. The third component weighed 5.2 mg. (33%) and had an ultraviolet absorption spectrum in agreement with that of C-curarine-III. It was purified further by a second chromatogram over powdered cellulose using a methyl ethyl ketone–methanol–water mixture (solvent C) to give 2.1 mg. of pure material. This was shown to be identical with an authentic sample of C-curarine-III by the following experiments. Comparative paper chromatograms using two different solvents—1-butanol and the solvent C (methyl ethyl ketone–methanol–water)—showed both to have identical behavior. Paper electrophoresis experiments both using 5% acetic acid and using a phosphate buffer (pH 6.8) showed no differences in behavior of the two compounds. Finally, the ultraviolet absorption spectra of the two samples were identical and both showed the same shift with base characteristic of C-curarine-III.

From the first fraction which moved with the solvent front there was isolated a solid residue. This was dissolved in water and made basic with ammonia. Extraction of the aqueous solution with chloroform gave 4.5 mg. of a solid which was taken up in solvent C and chromatographed over powdered cellulose. A compound showing pale-blue fluorescence moved with the solvent front. This showed only a slight movement on paper electrophoresis using either 5% acetic acid or a phosphate buffer (pH 6.8) and is presumed to be a tertiary base derived from the second half of des-C-curarine-I.

ROCHESTER, N. Y.

Syntheses of Thermochromic Ethylenes. A Study of the Relationship between Constitution and Thermochromism
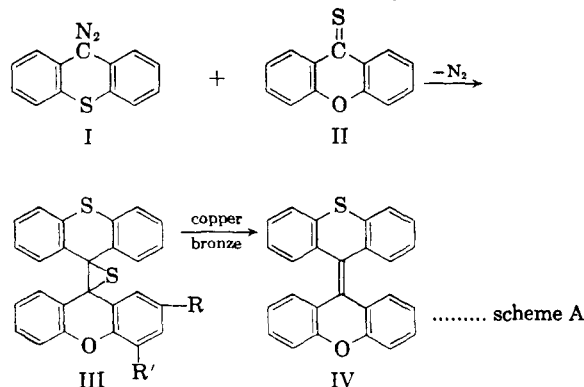
BY ALEXANDER SCHÖNBERG AND MAHMOUD MOHAMED SIDKY

A number of tetraarylethylenes were prepared by the ethylene sulfide method: the action of diaryldiazomethanes on diaryl thioketones yielded ethylene sulfides from which tetraarylethylenes were obtained by elimination of sulfur. Monothiodixanthylene (IV) shows thermochromic changes (colorless ⇌ deep green) at higher temperatures than dixanthylene (IV, S to be replaced by O). 9-(9-Fluorenylidene)-xanthene (VIIIa) is deep violet in color (non-thermochromic) in contrast to the yellow sulfur analog VIIIb, which is strongly thermochromic (yellow ⇌ malachite green); the green (thermochromic) form is believed to correspond to the violet form of (VIIIa). The relationship between thermochromic and adsorption colors of spiropyrans (comp. XIII) and dixanthylenes (comp. IV, O = S) is discussed.

In order to increase our knowledge of the relationship between thermochromic properties and constitution of tetraarylethylenes and thus to gain a better understanding of thermochromism, we have synthesized a number of new ethylenes, some of which showed strong thermochromic properties.

**Preparation of Ethylenes by the Ethylene Sulfide Method.**—Monothiodixanthylene(9-(thiaxanthene-10-ylidene)-xanthene) (IV) was obtained according to scheme A. Similarly dithiodixanthylene (IV, O = S) was prepared from diazothiaxanthene (I) and thiaxanthione (Vb).

The action of thiaxanthione (Vb) on diazothiaxanthene (I) yielded III (replace O by S; R = R' = H); using I and 2-methylxanthione (V, A = O, R = CH₃, R' = H) or 4-methylxanthione (V, A = O, R = H, R' = CH₃), the ethylene sulfide derivatives III (R = CH₃, R' = H) and III (R = H, R' = CH₃) were obtained, respectively.

By reactions similar to scheme A, xanthione (Va) and 9-diazofluorene (VI) yielded 9-(9-fluorenylidene)-xanthene (VIIIa), whereas 10-(9-fluorenylidene)-thiaxanthene (VIIIb) was obtained[1] from thiaxanthione (Vb) and 9-diazofluorene. Derivatives of VII also were prepared, e.g., by the action of 9-diazofluorene on 2-methylxanthione (Va, R = CH₃, R' = H) and on 4-methylxanthione (Va, R = H, R' = CH₃).

(1) It should be noted that in xanthenes the oxygen atoms have number 10, whereas the sulfur atoms in thiaxanthenes have the number 5.

.... scheme A

We also have obtained 3,3'-diphenylspiro-(thia-xanthene-10,2'-thiirane) (IX) by the action of diphenyldiazomethane on thiaxanthione (Vb); IX

V–VIIIa, A = O, R = R' = H
b, A = S, R = R' = H
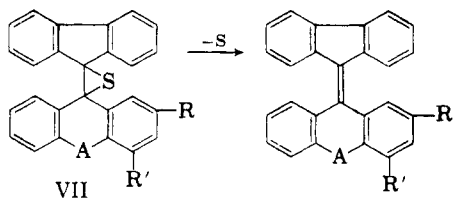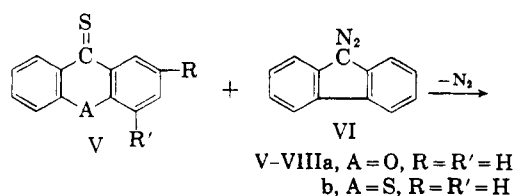
VIIIa, deep violet (non-thermochromic)
b, yellow (strong thermochromic,
yellow ⇌ malachite green)

yielded 10-(diphenylmethylene)-thiaxanthene (X) when reduced with zinc dust and acetic acid in the presence of concentrated hydrochloric acid; X was found to be identical with 9-benzhydrylidene-thioxanthene prepared by Bergmann and Corte[2] using a different method.
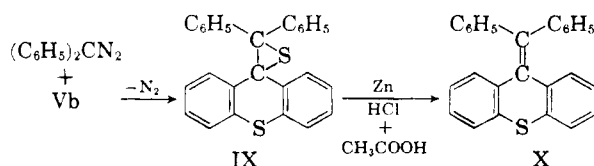
Attempts to prepare 2-phenyl-2-(9-xanthenyli-dene)-acetophenone (XI) by the action of azibenzil ($C_6H_5COCN_2C_6H_5$) on xanthione (II) according to scheme A met with difficulties and were discontinued when it was found that XI could be prepared by the action of 9,9-dichloroxanthene on desoxybenzoin; XI was found to be thermochromic (colorless ⇌ orange).[2a]

(2) E. Bergmann and H. Corte, *Ber.*, **66**, 39 (1933).

(2a) Addendum (Dec. 13, 1958): The thermochromism of XI is not unexpected in view of the thermochromic properties of 9-(diphenylmethylene)-xanthene (X, replace S by O) (A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **76**, 4134 (1954)). Both compounds belong to the group of overcrowded substances and their thermochromism should be classified as "conformation thermochromism of overcrowded molecules"—the concentration of various conformations being a function of temperature, resonance and in consequence color being related to the geometry of the molecules, *e.g.*, its planarity.

In accordance with this conception is the lack of thermochromic properties of 9-(phenylmethylene)-xanthene since its molecules are much less overcrowded than those of 9-(diphenylmethylene)-xanthene.

Similar observations have been made with 10-diphenylmethylene-anthrone (XIVc) (thermochromic) and 10-benzylideneanthrone (XIVa) (non-thermochromic) and the thermochromism of the former should be classified accordingly. Contrary to this view is a finding (V. M. Ingram, *J. Chem. Soc.*, 2322 (1950)) that 10-*m*-nitrobenzyli-deneanthrone (XIVb) exhibits "pronounced thermochromism."

Compound XIVb after five crystallizations from glacial acetic acid showed—as was to be expected—no thermochromic properties; crystals and solutions (phenetole, dimethylphthalate) were yellow (greenish tint) in the cold and showed this color also after heating.
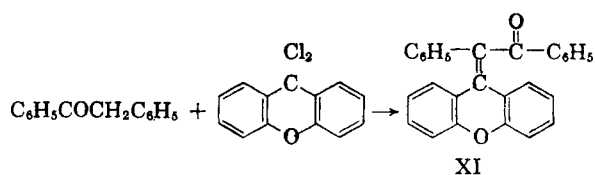
Thermochromic Properties of Pyran and Thia-pyran Derivatives.

—The detrimental effect of the replacement of oxygen by sulfur on the thermochromic properties is evident: 9-(diphenylmethylene)-xanthene (XI, C_6H_5CO- to be replaced by C_6H_5) is a strongly thermochromic substance,[3] colorless at room temperature but orange when molten. 10-(Diphenylmethylene)-thiaxanthene (X) is weakly thermochromic (colorless at room temperature and yellow when molten). Dixanthylene (IV, replace S by O) is colorless at liquid air temperature, turns blue-greenish on heating and its melt is deep blue-green. Monothiodixanthylene (IV) is colorless with yellow melt becoming deep green at 320°; thermochromic changes occur at higher temperatures than in the case of dixanthylene. Dithiodixanthylene (IV, replace O by S) is non-thermochromic.

Special attention is drawn to the fact that 9-(9-fluorenylidene)-xanthene (VIIIa) is deep violet in color and non-thermochromic in contrast to the sulfur analog VIIIb, which is yellow and melts with a malachite green color and solidifies on cooling, forming yellow crystals. The green form of VIIIb must be regarded as corresponding to VIIIa, the molecule of the latter having at room temperature and below a geometry (configuration) which can only be gained by its thia-analog VIIIb at higher temperatures.

The detrimental influence of the replacement of oxygen by sulfur on thermochromic properties has also been observed in the case of xantho-β-naphtho-spiropyran (XII)[4] (A = O), which is colorless. Its solutions in anisole are pink at 153°, the corresponding sulfur compound XII (A = S) is colorless, and its solutions in anisole are colorless at 153°, though in boiling diphenyl ether (b.p. 259°) or tetralin (b.p. 207°) a pink color is produced which disappears on cooling.

XII   XIII
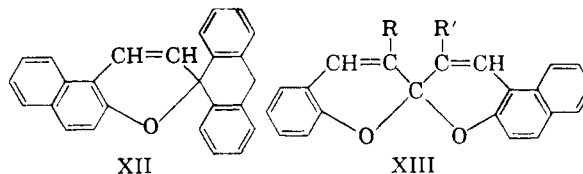
Development of Thermochromic Colors by Adsorption.

—There is an unexpected relationship between the thermochromism of dixanthylenes and of spiropyrans, namely, the development of thermo-

These experiments were carried out with K.-H. Brosowski, Dept. of Organic Chemistry, Technische Universität Berlin (West).
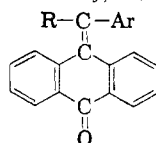
XIVa, Ar = C_6H_5, R = H
b, Ar = $C_6H_4NO_2$-m, R = H
c, Ar = R = C_6H_5

(3) A. Schönberg and S. Nickel, *Ber.*, **62**, 2323 (1931).

(4) A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **74**, 5640 (1952); A. Mustafa, *J. Chem. Soc.*, 2295 (1949).

chromic colors by adsorption. Thus the colorless 3-methylbenzo-β-naphthospiran (XIII, R = CH₃, R' = H) yields violet solutions in hot anisole and gives a blue adsorbate on silica gel and alumina. By contrast 3'-methylbenzo-β-naphthospiran (XIII, R = H, R' = CH₃) dissolves in hot inert solvents (e.g., benzene or anisol) without developing thermochromic colors, but the expected thermochromic colors are shown by the adsorbate on silica gel or alumina[5] (blue).

These observations should be linked with recent work by Kortüm, et al.,[6] who state that dithiodixanthylene (IV, O = S) which shows thermochromic properties neither in the solid state nor in solution, shows these properties when adsorbed on magnesium oxide.

It is worthwhile to point to the similarity of the thermochromic properties of spiropyrans and dixanthylenes which any theory of thermochromism must explain in order to be acceptable.

Experimental

Concd. sulfuric acid was used in the color test.

Thiaxanthione (Vb).—Two grams of thiaxanthone (I, N₂ to be replaced by O) and 2.5 g. of purified[7] phosphorus pentasulfide were refluxed with 40 ml. of toluene for 2 hours. The reaction mixture (green in color) was filtered while hot and the residue was extracted several times with hot benzene. The filtrate and the united extracts were evaporated to dryness and the residue (1.4 g.) was crystallized from petroleum ether (b.p. 100–120°), yielding brownish-green crystals of Vb, m.p. 170°; Arndt[8] reported m.p. 176° and Mayer[9] 172–175°.

Action of Diphenyldiazomethane on Thiaxanthione (Vb). —Diphenyldiazomethane (prepared from 4 g. of benzophenone hydrazone) in benzene was added to 1 g. of Vb. A vigorous evolution of gases occurred and the mixture was left overnight at room temperature. The benzene was left to evaporate at room temperature and the residue so obtained was washed several times with petroleum ether (b.p. 50–70°), then crystallized from petroleum ether (b.p. 110–120°), as colorless crystals of IX, m.p. 208° (not sharp). It gave no color with sulfuric acid, yield ca. 1 g. Anal. Calcd. for C₂₆H₁₈S₂: C, 79.1; H, 4.6; S, 16.2. Found: C, 79.1; H, 4.8; S, 16.0.

10-(Diphenylmethylene)-thiaxanthene (X).—One gram of IX was dissolved in hot glacial acetic acid (50 ml.) and about 2 g. of zinc dust was added, followed by a few drops of concentrated hydrochloric acid (sp. gr. 1.18). The mixture was refluxed for 1.5 hours and filtered while hot. The solution was concentrated and the crystals of X that separated were collected and recrystallized from petroleum ether (b.p. 100–120°). Another crop was obtained by extracting the solid substance contaminated with inorganic matter with petroleum ether (b.p. 100–120°); X was obtained as colorless crystals, m.p. 248°, yellow melt which became colorless again on cooling. Bergmann[2] gave m.p. of 243° from amyl alcohol. Anal. Calcd. for C₂₆H₁₈S: S, 8.8. Found: S, 9.1.

2-Methylxanthione (Va, R = CH₃, R' = H).—Two grams of 2-methylxanthone[10] was heated with 2.5 g. of purified phosphorus pentasulfide until melted, and the mixture was kept at 120–125° for 2 hours. The solid mass obtained on cooling was powdered and extracted several times with hot benzene (ca. 60 ml. total). The benzene was evaporated and the solid residue was crystallized from petroleum ether (60–90°) as green crystals of 2-methylxanthione, m.p. 136°. It gave a deep yellow color with green fluorescence with sulfuric acid; yield ca. 1.4 g. Anal. Calcd. for C₁₄H₁₀OS: S, 14.1. Found: S, 14.1.

4-Methylxanthione (Va, R = H, R' = CH₃).—The same procedure using 4-methylxanthione[10] as described for the preparation of 2-methylxanthione was followed; Va (R = H, R' = CH₃) was obtained in brown crystals from petroleum ether (b.p. 60–90°), m.p. 128°. It gave a deep yellow color with sulfuric acid, yield ca. 1.4 g. Anal. Calcd. for C₁₄H₁₀OS: S, 14.1. Found: S, 14.0.

Action of 9-Diazofluorene (VI) on (a) Thiaxanthione (Vb).—Thiaxanthione (1 g.) and 9-diazofluorene[11] (1.4 g.) were dissolved in about 30 ml. of benzene (thiophene-free and dried over sodium). A brisk evolution of gases occurred and the solution became pale orange in color. The reaction was completed by refluxing on a boiling water-bath for 2 hours. The crystals of VIIb (1 g.), that separated on addition of petroleum ether (b.p. 50–70°) to the cooled mixture were collected, washed with petroleum ether and crystallized from benzene as colorless crystals, m.p. 240° dec. It gave no color with sulfuric acid. Anal. Calcd. for C₂₆H₁₆S₂: C, 79.6; H, 4.1; S, 16.3. Found: C, 79.3; H, 4.1; S, 16.0.

(b) Xanthione (II).—Xanthione (1 g.) was dissolved with about 1.5 g. of 9-diazofluorene in 30 ml. of dry benzene. The benzene solution was refluxed for 3 hours, then concentrated in vacuum and cooled. The crystals of VIIa that separated (ca. 1 g.) on adding petroleum ether (b.p. 50–70°), were collected, washed with petroleum ether and crystallized from benzene as colorless crystals, m.p. 198° (became violet at 160°). A violet color is produced with sulfuric acid. Anal. Calcd. for C₂₆H₁₆OS: C, 83.0; H, 4.2; S, 8.5. Found: C, 83.1; H, 4.1; S, 8.2.

(c) 2-Methylxanthione (Va, A = O, R = CH₃, R' = H). —The same procedure was carried out as in the case of xanthione; VII (R = CH₃, R' = H) was obtained as colorless crystals from benzene–petroleum ether (b.p. 50–70°), m.p. 168° (became violet at 140°). It gave a violet color with sulfuric acid, yield ca. 0.7 g. Anal. Calcd. for C₂₇H₁₈OS: C, 83.1; H, 4.6; S, 8.2. Found: C, 83.0; H, 4.7; S, 7.5.

(d) 4-Methylxanthione (Va, R = H, R' = CH₃).—The action of 9-diazofluorene on 4-methylxanthione as described above, gave VII (R = H, R' = CH₃) as almost colorless crystals from benzene–petroleum ether (b.p. 50–70°), m.p. 184° (violet at 150°). It gave a deep violet color with sulfuric acid, yield ca. 0.7 g. Anal. Calcd. for C₂₇H₁₈OS: C, 83.1; H, 4.6; S, 8.2. Found: C, 83.4; H, 4.8; S, 8.4.

9-Diazothiaxanthene (I).—The method described by Schönberg and Stolpp[12] for the preparation of 9-diazothiaxanthene was modified. Thiaxanthone hydrazone (4 g.), yellow mercuric oxide (8 g.) and anhydrous sodium sulfate (2 g.) were ground together, then transferred to a dry, glass-stoppered bottle, and dry ether (50 ml.) was added. About 0.5 ml. of saturated solution of potassium hydroxide in absolute ethyl alcohol was added, and the whole was shaken for 40 minutes. The violet-blue ethereal solution was filtered and concentrated in vacuum, whereupon green crystals of 9-diazothiaxanthene separated, m.p. 105° with a red melt, yield was ca. 2 g.

Action of 9-Diazothiaxanthene (I) on (a) Thiaxanthione (Vb).—Thiaxanthione (1 g.) was dissolved with 9-diazothiaxanthene (1.5 g.) in about 30 ml. of dry benzene. A brisk evolution of nitrogen occurred and the benzene solution became pale in color. The reaction mixture was completed by heating on a boiling water-bath for 2 hours. The solution was concentrated in vacuum to about one-third of its volume and petroleum ether (b.p. 50–70°) was added. The yellow crystals of III (replace O by S, R = R' = H) that separated, were collected and washed with petroleum ether, then recrystallized from benzene as yellow crystals, no sharp m.p. up till 350°. It gave a red color with sulfuric acid, yield ca. 1 g. Anal. Calcd. for C₂₆H₁₆S₃: C, 73.6; H, 3.8; S, 22.6. Found: C, 73.8; H, 3.8; S, 22.4.

(b) Xanthione (II).—Xanthione (1 g.) together with 9-diazothiaxanthene (1.5 g.), was dissolved in about 30 ml. of dry benzene and worked as above; III (R = R' = H was obtained as colorless crystals from benzene–petroleum ether (b.p. 50–70°), m.p. 205° dec. It gave a red color with sulfuric acid, yield ca. 0.6 g. Anal. Calcd. for C₂₆H₁₆OS₂: C, 76.4; H, 3.9; S, 15.7. Found: C, 76.4; H, 4.0; S, 15.4.

(5) A. Schönberg, A. Mustafa and W. Asker, THIS JOURNAL, **73**, 2876 (1951).

(6) G. Kortüm, W. Theilacker and G. Schreyer, Z. physik. Chem. Neue Folge, **11**, 182 (1957).

(7) W. Baker, J. Harborne and W. Ollis, J. Chem. Soc., 1303 (1952).

(8) F. Arndt and L. Lorenz, Ber., **63**, 3121 (1930).

(9) R. Mayer, ibid., **90**, 2362 (1958).

(10) F. Ullmann and M. Zlokasoff, ibid., **38**, 2111 (1905).

(11) A. Schönberg, W. Awad and N. Latif, J. Chem. Soc., 1368 (1951).

(12) A. Schönberg and Th. Stolpp, Ber., **63**, 3102 (1930).

(c) 2-Methylxanthione (Va, R = CH₃, R' = H).—The same procedure described in the case of xanthione was followed; III (R = CH₃, R' = H) was obtained as almost colorless crystals from benzene–petroleum ether (b.p. 50–70°), m.p. 210° dec. It gave a red color with sulfuric acid, yield *ca.* 0.5 g. *Anal.* Calcd. for C₂₇H₁₈OS₂: C, 76.8; H, 4.3; S, 15.1. Found: C, 76.4; H, 4.3; S, 15.0.

(d) 4-Methylxanthione (Va, R = H, R' = CH₃).—Compound III (R = H, R' = CH₃) was obtained as yellow crystals from petroleum ether (100–120°), m.p. 190° dec. It gave a red color with sulfuric acid, yield *ca.* 0.4 g. *Anal.* Calcd. for C₂₇H₁₈OS₂: C, 76.8; H, 4.3; S, 15.1. Found: C, 76.6; H, 4.3; S, 14.9.

Action of Copper Bronze on (a) VIIb.—Compound VIIb (0.5 g.) was heated together with 0.5 g. of copper bronze in vacuum (oil-pump) at 240–250° (bath temperature) for 30 minutes. The solid substance that remained at the bottom of the flask was extracted with boiling xylene and the crystals that separated on cooling (yield *ca.* 0.3 g.) were recrystallized from xylene as yellow crystals of VIIIb, m.p. 245°, which gave no color with sulfuric acid. *Anal.* Calcd. for C₂₆H₁₆S: C, 86.6; H, 4.5; S, 8.9. Found: C, 86.5; H, 4.6; S, 8.5.

When the substance (in a capillary tube) was heated to within a few degrees above its m.p., it gave a deep green melt, which on cooling formed yellow crystals, which in turn gave the green melt on heating.

(b) VIIa.—Compound VIIa (0.5 g.) was heated with 0.5 g. of copper bronze in vacuum (oil-pump) for 20 minutes at 210° (bath temperature). The deep violet substance at the bottom of the flask was extracted with boiling xylene. When the xylene solution was cooled, it gave crystals of VIIIa (yield *ca.* 0.3 g.) which were recrystallized from xylene as deep violet crystals, m.p. 240°, which gave an orange color with sulfuric acid. *Anal.* Calcd. for C₂₆H₁₆O: C, 90.6; H, 4.7. Found: C, 90.3; H, 4.7.

(c) III.—One gram of III (replace O by S, R = R' = H), mixed with 1 g. of copper bronze, was heated together in vacuum (oil-pump) at about 340° (bath temperature) for one hour. The solid substance at the bottom of the flask was extracted with hot xylene, the xylene solution on cooling, deposited colorless crystals (yield *ca.* 0.7 g.) of IV[13] (replace O by S) which were recrystallized from xylene several times as colorless crystals, m.p. above 350°. *Anal.* Calcd. for C₂₆H₁₆S₂: S, 16.3. Found: S, 16.0.

(d) III.—One gram of III (R = R' = H), mixed with 1 g. of copper bronze, was heated in vacuum (oil-pump) at 220–230° (bath temperature) for 30 minutes. The solid substance at the bottom of the flask was extracted with hot benzene; the solution on cooling deposited crystals of IV (yield *ca.* 0.6 g.) which were recrystallized from benzene as colorless crystals, m.p. 295°, yellow melt which became deep green at about 320° and on cooling, and solidified to colorless crystals. It gave no color with sulfuric acid. *Anal.* Calcd. for C₂₆H₁₆OS: C, 83.0; H, 4.2; S, 8.6. Found: C, 83.0; H, 4.4; S, 8.5.

2-Phenyl-2-(9-xanthylidene)-acetophenone (XI).—Xanthone (2.5 g.) was refluxed with 30 ml. of thionyl chloride for 15 hours (calcium chloride tube), the excess of thionyl chloride was distilled off and the orange-red oil that remained was dissolved in 20 ml. of dry benzene, then treated with 1 g. of desoxybenzoin in 20 ml. of dry benzene. The reaction mixture was refluxed for 10 hours (calcium chloride tube) till the evolution of hydrogen chloride ceased. It was concentrated and then petroleum ether (50–70°) was added. The crystals of XI that separated were crystallized from petroleum ether (b.p. 100–120°) as colorless crystals, m.p. 174°; the orange melt gave colorless crystals on cooling. It gave an olive-green color with sulfuric acid, yield *ca.* 0.8 g. *Anal.* Calcd. for C₂₇H₁₈O₂: C, 86.6; H, 4.9. Found: C, 86.3; H, 4.9.

(13) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 305 (1944).

CAIRO, U.A.R. (EGYPT)

Rearrangement of the 2-Phenylethyl Free Radical

BY LYNN H. SLAUGH

The 2-phenylethyl-1-C¹⁴ radical, produced by the peroxide-catalyzed decarbonylation of 3-phenylpropionaldehyde-2-C¹⁴ has been shown (by tracer techniques) to undergo partial rearrangement to the 2-phenylethyl-2-C¹⁴ radical. Added mercaptan decreases the extent of rearrangement. It has also been shown that the 2-phenylethyl radical does not rearrange to the 1-phenylethyl radical *via* a 1,2-hydrogen atom migration.

Introduction

Several free radicals have been shown to undergo carbon-to-carbon phenyl migration. The first report of such a rearrangement was by Kharasch and Urry[1] who found that the 2-methyl-2-phenylpropyl (neophyl) radical underwent partial rearrangement to the 1-benzyl-1-methylethyl radical. Winstein and Seubold[2] confirmed this observation when they discovered that the decarbonylation of 3-phenyliso-valeraldehyde led to approximately equal amounts of isobutylbenzene and *t*-butylbenzene. Later Curtin and Hurwitz[3] studied the peroxide-catalyzed free radical decarbonylation of four additional aldehydes and found that the radicals resulting from the decarbonylation of 3,3,3-triphenylpropionaldehyde, 2-methyl-3,3,3-triphenylpropionaldehyde and 3,3-diphenylbutyraldehyde underwent 100% 1,2-phenyl migration as determined by the structures of

the products. However, 3-*p*-anisyl-3-phenylpropionaldehyde gave predominantly 1-*p*-anisyl-1-phenylethane, indicating that the carbon skeleton did not rearrange extensively (<15%). Curtin and Hurwitz[3] suggested that the 2-*p*-anisyl-2-phenylethyl radical may have undergone a 1,2-hydrogen migration (equation 1).

$$\underset{\text{Ph}}{CH_3OC_6H_4\overset{|}{C}HCH_2\cdot} \longrightarrow \underset{\text{Ph}}{CH_3OC_6H_4\overset{|}{C}CH_3} \quad (1)$$
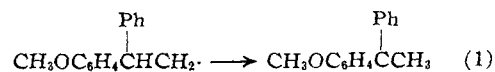
Kharasch, Lambert and Urry[4,5] also have postulated 1,2-hydrogen migrations in free radicals because the principal unsaturated products from the disproportionations of the 3-phenylpropyl and *n*-butyl radicals were found to be, respectively, *trans*-β-methylstyrene (rather than allylbenzene) and *trans*-2-butene (rather than 1-butene).

(1) M. S. Kharasch and W. H. Urry, THIS JOURNAL, 66, 1438 (1944).

(2) S. Winstein and F. H. Seubold, *ibid.*, 69, 2916 (1947).

(3) D. Y. Curtin and M. J. Hurwitz, *ibid.*, 74, 5381 (1952).

(4) M. S. Kharasch F. L. Lambert and W. H. Urry, *J. Org. Chem.*, 10, 298 (1945).

(5) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 126.