(c) **2-Methylxanthione** (Va, R = CH_3, R′ = H).—The same procedure described in the case of xanthione was followed; III (R = CH_3, 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 $C_{27}H_{18}OS_2$: 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′ = CH_3).—Compound III (R = H, R′ = CH_3) 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 $C_{27}H_{18}OS_2$: 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 $C_{26}H_{16}S$: 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 $C_{26}H_{16}O$: 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 $C_{26}H_{16}S_2$: 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 $C_{26}H_{16}OS$: 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 $C_{27}H_{18}O_2$: C, 86.6; H, 4.9. Found: C, 86.3; H, 4.9.

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

CAIRO, U.A.R. (EGYPT)

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Rearrangement of the 2-Phenylethyl Free Radical

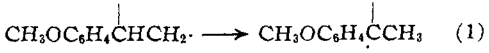
BY LYNN H. SLAUGH

RECEIVED OCTOBER 29, 1958

The 2-phenylethyl-1-C^{14} radical, produced by the peroxide-catalyzed decarbonylation of 3-phenylpropionaldehyde-2-C^{14} has been shown (by tracer techniques) to undergo partial rearrangement to the 2-phenylethyl-2-C^{14} 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-phenylisovaleraldehyde 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).



$$CH_3OC_6H_4\overset{\overset{\displaystyle Ph}{|}}{C}HCH_2\cdot \longrightarrow CH_3OC_6H_4\overset{\overset{\displaystyle Ph}{|}}{C}CH_3 \quad (1)$$

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).

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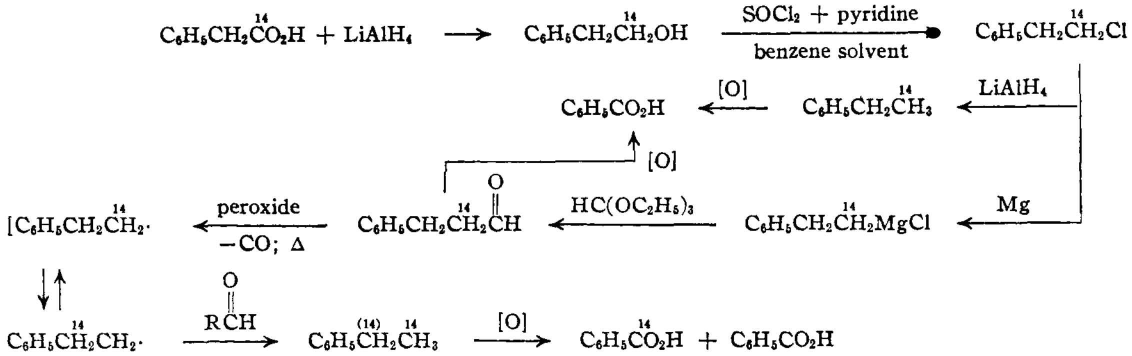
[1] M. S. Kharasch and W. H. Urry, THIS JOURNAL, **66**, 1438 (1944).

[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 Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 126.



However, others have reported that hydrogen atoms failed to migrate. Kornblum and De La Mare,[6] and Kornblum and Oliveto[7] concluded that alkoxy radicals of the type $R\overset{R'}{\underset{H}{C}}O\cdot$ do not rearrange to $R\overset{R'}{\dot{C}}OH$ even when R is a phenyl group. Brown and Russell[8] found also that the isobutyl radical does not rearrange (1,2-hydrogen migration) to the *t*-butyl radical during the photochlorination of isobutane. This is not surprising, however, since a phenyl group will not migrate during the photochlorination of *t*-butylbenzene.[9,10]

The phenyl migrations thus far reported have involved the rearrangement of a less stable radical to a more stable radical, *i.e.*, primary to tertiary, etc. In each instance the rearrangement also has been in the direction to relieve steric compression of the substituent groups on the carbon atom adjacent to the free radical.

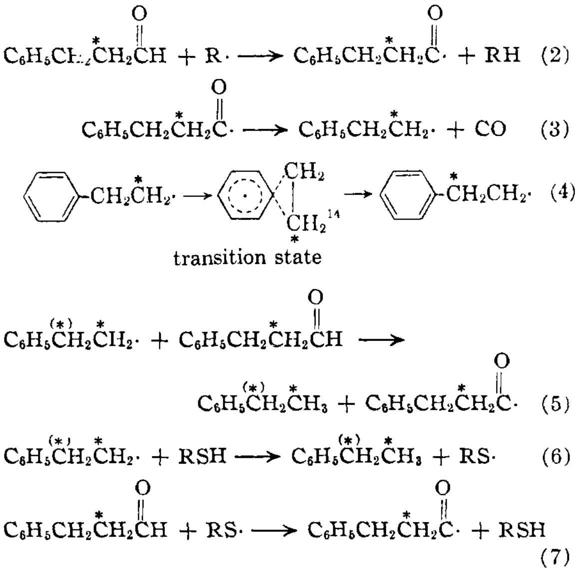
The purpose of this communication is to report the partial rearrangement (1,2-phenyl migration) of the 2-phenylethyl-1-C^{14} radical. This rearrangement proceeds despite the fact that no relief of steric compression nor ultimate change in radical stability is involved, *i.e.*, a primary radical rearranges to a primary radical. In addition, the possibility of hydrogen atom migration in the 2-phenylethyl radical has been studied.

Results and Discussion

The extent to which the 2-phenylethyl-1-C^{14} radical (produced by the decarbonylation of 3-phenylpropionaldehyde-2-C^{14}) rearranges to the 2-phenylethyl-2-C^{14} radical was ascertained by determining the relative amounts of 2-phenylethane-1-C^{14} and 1-phenylethane-1-C^{14} in the product. This was accomplished simply by comparing the C^{14} activity of the ethylbenzene-C^{14} and the benzoic acid-C^{14} obtained upon oxidation of the ethylbenzene-C^{14}.

The reaction scheme summarizes the syntheses and degradations which are utilized in this study. The benzoic acid resulting from the oxidation of the 3-phenylpropionaldehyde-2-C^{14} did not have any detectable C^{14} activity, indicating that rearrangement did not occur in any step of the synthesis.[11] The possibility of rearrangement during the permanganate oxidation of phenylethane-C^{14} (resulting from the decarbonylation of 3-phenylpropionaldehyde-2-C^{14}) could be excluded since the oxidation of 2-phenylethane-1-C^{14} (obtained by the reduction of 2-phenylethyl chloride-1-C^{14}) gave inactive benzoic acid. It is concluded, therefore, that the rearrangements reported in Table I result from the rearrangement of the 2-phenylethyl-1-C^{14} radical itself and not from any other source. All the decarbonylations were carried out in a one molar solution of *o*-dichlorobenzene using di-*t*-butyl peroxide as catalyst.

Rearrangement of the 2-Phenylethyl-1-C^{14} Radical.—The mechanism[12] (2) to (7) is useful in interpreting the results listed in Table I where the asterisk indicates C^{14}



$$C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}H + R\cdot \longrightarrow C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}\cdot + RH \quad (2)$$

$$C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}\cdot \longrightarrow C_6H_5CH_2\overset{*}{C}H_2\cdot + CO \quad (3)$$

(4)

transition state

$$C_6H_5\overset{(*)}{C}H_2\overset{*}{C}H_2\cdot + C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}H \longrightarrow C_6H_5\overset{(*)}{C}H_2\overset{*}{C}H_3 + C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}\cdot \quad (5)$$

$$C_6H_5\overset{(*)}{C}H_2\overset{*}{C}H_2\cdot + RSH \longrightarrow C_6H_5\overset{(*)}{C}H_2\overset{*}{C}H_3 + RS\cdot \quad (6)$$

$$C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}H + RS\cdot \longrightarrow C_6H_5CH_2\overset{*}{C}H_2\overset{O}{\overset{\|}{C}}\cdot + RSH \quad (7)$$

Although the extent of rearrangement of the 2-phenylethyl-1-C^{14} radical is less (2.3–5.1%) than that of the neophyl radical[12b] (~80%) under similar conditions, it illustrates that the relief of steric compression or the formation of a more stable re-

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[6] N. Kornblum and H. E. De La Mare, THIS JOURNAL, **74**, 3079 (1952).

[7] N. Kornblum and E. Oliveto, *ibid.*, **71**, 226 (1949).

[8] H. C. Brown and G. A. Russell, *ibid.*, **74**, 3995 (1952).

[9] M. S. Kharasch and H. C. Brown, *ibid.*, **61**, 2142 (1939).

[10] G. A. Russell and H. C. Brown, *ibid.*, **74**, 3995 (1952).

[11] C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, **32**, 1005 (1954), previously demonstrated that 2-phenylethanol-1-C^{14} could be converted to 2-phenylethyl chloride-1-C^{14} using thionyl chloride in pyridine. Without the pyridine, however, extensive rearrangement occurs.

[12] (a) Similar to that proposed by Seubold and Urry and Nicolaides for the neophyl radical, but extended to include the function of added mercaptans. (b) F. H. Seubold, Jr., THIS JOURNAL, **75**, 2532 (1953). (c) W. H. Urry and N. Nicolaides, *ibid.*, **74**, 5163 (1952).

TABLE I

DECARBONYLATION OF 3-PHENYLPROPIONALDEHYDE-2-C^{14}

Experiment	1	2	3	4
Temperature, °C.	150–155	165–175	145–150	165–170
Thiophenol, mole % of aldehyde	2.4	2.4	0.0	0.0
Decomposition of aldehyde,[a] %	76.3	75.8	67.8	69.4
C^{14} Activity[b] of ethylbenzene,[c] d.p.m./mmole	7760 ± 80	7665 ± 77	3625 ± 36	3588 ± 36
C^{14} Activity[b] of benzoic acid,[d] d.p.m./mmole	180 ± 4	322 ± 5	120 ± 2	183 ± 4
Rearrangement, %	$2.3_2 \pm 0.1$	$4.2_1 \pm 0.1$	$3.3_1 \pm 0.1$	$5.1_0 \pm 0.1$

[a] Based on carbon monoxide evolved. [b] The reported deviations of the C^{14} activities (disintegrations per minute per millimole) are standard deviations of several counts of the same sample. In some instances duplicate samples were measured. [c] Ethylbenzene-C^{14} obtained from the decarbonylation of 3-phenylpropionaldehyde-2-C^{14}. [d] Benzoic acid-C^{14} obtained by the oxidation of the above ethylbenzene-C^{14}.

arranged radical under rate-limiting conditions could be important only if there is considerable bond breaking in the transition state (equation 4). The rearrangement of the 2-phenylethyl-1-C^{14} radical, as well as those of other radicals, likely is assisted by the delocalization of its odd electron on the aromatic ring (equation 4) in the transition state.

Seubold[12] found that the amount of rearrangement of the neophyl radical was not altered very much by a change in reaction temperature. This indicates that the energies of activation for the two competing reactions, *i.e.*, rearrangement and hydrogen abstraction, are approximately equal (~8 kcal./mole). However, the amount of rearrangement of the 2-phenylethyl-1-C^{14} radical increases significantly with temperature (Table I) indicating that the energy of activation for rearrangement (equation 4) is greater than that for the abstraction of a hydrogen (equation 5).

Effects of Added Mercaptan.—Harris and Waters[13] reported that the addition of 0.5 mole % of benzylmercaptan greatly increased the extent of the free radical-catalyzed decomposition of aliphatic aldehydes. The data in Table I show that the addition of 2.4 mole % of thiophenol reduces the amount of rearrangement by approximately 30% (compare experiment no. 1 with 3 and 2 with 4). The chain transfer constants for mercaptans[14,15] in the polymerization of styrene are much greater than those for aldehydes,[16] indicating that mercaptans donate hydrogen atoms to free radicals much more rapidly than do aldehydes. Therefore the amount of rearrangement of the 2-phenylethyl-1-C^{14} radical decreased because the hydrogen abstraction step (equation 6) now competed more favorably with the rearrangement reaction (equation 4). In other words, the greater hydrogen donor ability of the mercaptan decreases the life time of the 2-phenylethyl-1-C^{14} radical and consequently the amount of rearrangement. In support of this, it was found that tritium was incorporated into the side chain of the product ethylbenzene (see Table II) when 3-phenylpropionaldehyde was decarbonylated in the presence of benzyl mercaptan-S-*t* (see below).

Hydrogen Migration in the 2-Phenylethyl Radical.—The peroxide-catalyzed decarbonylation of 3-phenylpropionaldehyde was carried out in the presence of benzyl mercaptan-S-*t* and *n*-propylbenzene. A hydrogen atom migration in the 2-phenylethyl radical would produce the 1-phenylethyl radical (equation 8) which would give ethylbenzene-α-*t*

$$C_6H_5CH_2CH_2\cdot \longrightarrow C_6H_5\dot{C}HCH_3 \qquad (8)$$

upon reaction with the benzylmercaptan-S-*t* (equation 9).

$$C_6H_5\dot{C}HCH_3 + C_6H_5CH_2ST \longrightarrow C_6H_5CHTCH_3 + C_6H_5CH_2S\cdot \qquad (9)$$

Likewise, the 2-phenylethyl radical without hydrogen migration would give only ethylbenzene-β-*t*. The resulting ethylbenzene-*t* was allowed to react with a stoichiometric quantity of N-bromosuccinimide; the tritium activity of the resultant succinimide (see Table II) was thus a measure of the amount of ethylbenzene-α-*t* present (equation 10)

$$C_6H_5CHTCH_3 + C_4H_4O_2NBr \xrightarrow{\text{light}} C_6H_5CHBrCH_3 + C_4H_4O_2NT \qquad (10)$$

TABLE II

DECARBONYLATION OF 3-PHENYLPROPIONALDEHYDE IN THE PRESENCE OF BENZYL MERCAPTAN-S-*t* AND *n*-PROPYLBENZENE AT 140–150°

Compound	Initial molarity	Tritium activity[b] d.p.m./mmole	Ethylbenzene-*t* activity, %
3-Phenylpropionaldehyde[a]	1.0	....	..
Benzyl mercaptan-S-*t*	0.09	271,000	..
n-Propylbenzene-*t*[c]	.52	371 ± 2	7.7
Ethylbenzene-*t*	.0	4,847 ± 33	..
Succinimide-*t*	.0	22 ± 1	0.45

[a] Based on the carbon monoxide evolved, 26.4% of the aldehyde underwent decarbonylation during the reaction. [b] The deviations of the tritium activities (disintegrations per minute per millimole) are standard deviations of several counts of the same sample. Duplicate samples were also counted. [c] The *n*-propylbenzene had zero activity before the reaction.

The succinimide was found to have activity only 0.45% as great as that of the ethylbenzene-*t* recovered from the decarbonylation reaction. Since the ratio of hydrogen abstraction to tritium abstraction from ethylbenzene-α-*t* by the succinimidyl radical (the tritium isotope effect) is approximately 4.0,[17] the amount of ethylbenzene-α-*t* present is calculated to be 1.8% of the total ethylbenzene-*t*. It is believed, however, that tritium activity was not the result of a hydrogen migration but rather the result of exchange with the mercaptan. The

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(13) E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952).

(14) C. Walling, THIS JOURNAL, **70**, 2561 (1948).

(15) R. A. Gregg, D. M. Alderman and F. R. Mayo, *ibid.*, **70**, 3740 (1948).

(16) R. A. Gregg and F. R. Mayo, *ibid.*, **75**, 3530 (1953).

(17) (a) Estimated from the deuterium isotope effect for the same reaction, 2.6 ± 0.04, as observed by K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958). (b) Method of estimation is that of C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *ibid.*, **80**, 5885 (1958).

fact that the *n*-propylbenzene which had been included in the reaction mixture possess 7.7% as much activity as the ethylbenzene-*t* (Table II) showed that hydrogen exchange between the alkyl side chains and the mercaptan was occurring. This higher value, *i.e.*, 7.7% as compared to 1.8%, can easily be accounted for since the *n*-propylbenzene concentration was always more than twice that of the ethylbenzene-*t*. In addition, the exchange of all of the seven exchangeable hydrogens in *n*-propylbenzene was measured, whereas exchange of only the two α-hydrogens in ethylbenzene-*t* was determined by reaction with N-bromosuccinimide. It is apparent also that hydrogen exchange in the 3-position of 3-phenylpropionaldehyde was not extensive before decarbonylation.[18]

These results support the contention that hydrogen atoms do not readily undergo 1,2-shifts. It is felt, therefore, that the 1,2-hydrogen migrations suggested by Curtin and Hurwitz[3] (equation 1) for the 2-*p*-anisyl-2-phenylethyl radical[19] and by Kharasch and Lambert[4,5] for the 3-phenylpropyl and *n*-butyl radicals probably do not occur. The *trans*-β-methylstyrene (rather than allylbenzene) and *trans*-2-butene (rather than 1-butene) obtained from the disproportionation of the above radicals may be the result of double bond isomerization rather than 1,2-hydrogen migrations.

Experimental[20]

2-Phenylethanol-1-C^{14}.—Phenylacetic-1-C^{14} (0.05 mc., purchased from Nuclear-Chicago Corporation) was diluted to 60 g. with Eastman Kodak Co. phenylacetic acid.

After filtering, washing with water and drying, the phenylacetic acid-1-C^{14} (40.7 g., 0.3 mole) was reduced with lithium aluminum hydride in ether solution according to the procedure of Nystrom and Brown.[21] The resulting salts were dissolved in excess 10% sulfuric acid, the ether layer washed repeatedly with dilute sodium carbonate solution and then water and finally dried over anhydrous potassium carbonate. After removal of the ether by distillation, the crude alcohol was dissolved in 100 ml. of benzene and again dried over anhydrous potassium carbonate.

2-Phenylethyl Chloride-1-C^{14}.—The crude alcohol from above was added dropwise over 45 minutes, while stirring, to a solution of 5 ml. of pyridine and 39.3 g. (0.33 mole) of thionyl chloride in 50 ml. of benzene (25°). After refluxing for one hour, the solution was cooled and treated with ice-water and the benzene layer collected. The water layer was extracted with additional benzene (50 ml.), after which the combined benzene extracts were washed with dilute sodium carbonate solution, then water, and dried over anhydrous potassium carbonate. Careful distillation gave 30.3 g. (0.216 mole) of 2-phenylethyl chloride-1-C^{14}, b.p. 94.4–94.7° (15 mm.), for an over-all yield of 72% from the acid.

3-Phenylpropionaldehyde-2-C^{14}.—The procedure used by Cohen[22] for the preparation of 3-phenylpropionaldehyde was employed. The magnesium Grignard reagent of 2-phenylethyl chloride-1-C^{14} (0.20 mole) was treated with triethyl orthoformate (0.20 mole) and the aldehyde recovered as the bisulfite adduct. Steam distillation of the bisulfite adduct from sodium carbonate solution gave 3-phenylpropionaldehyde-2-C^{14} which was diluted with 113 g. of unlabeled aldehyde and purified by distillation, b.p. 100–102° (13 mm.), $n^{20.0}\text{D}$ 1.5220.

Reduction of 2-Phenylethyl Chloride-1-C^{14}.—One gram of the above 2-phenylethyl chloride-1-C^{14} was diluted with 39 g. of unlabeled 2-phenylethyl chloride (Eastman Kodak Co.) and added to a solution of lithium aluminum hydride (7.6 g., 0.2 mole) and lithium hydride (1.6 g.) in 200 ml. of tetrahydrofuran (freshly distilled from lithium aluminum hydride). The mixture was refluxed for 12 hours with stirring, then cooled, hydrolyzed with water and the resulting salts dissolved with cold 10% sulfuric acid. The product was extracted with *n*-pentane, washed with water, dried over anhydrous calcium chloride, and distilled through an efficient column giving 2-phenylethane-1-C^{14} (17.6 g., 58.3% yield), b.p. 135.5–136.0°, $n^{20}\text{D}$ 1.4950. Analysis by gas chromatography indicated the 2-phenylethane-1-C^{14} was at least 98% pure. The C^{14} activity was found to be 7.27 × 10^{3} d.p.m./mmole.

Oxidation of 2-Phenylethane-1-C^{14}.—Potassium permanganate (23.8 g., 0.15 mole), 2-phenylethane-1-C^{14} (4.0 g., 0.038 mole), water (200 ml.) and 5 ml. of 25% sodium hydroxide were refluxed, with stirring, until the permanganate color had disappeared. The basic solution was cooled, filtered and extracted repeatedly with *n*-pentane to remove any unreacted 2-phenylethane-1-C^{14} which might contaminate the benzoic acid. The benzoic acid (2.5 g., 66% yield) obtained upon acidification of the basic solution was recrystallized twice from a *n*-pentane–methylene chloride solution, m.p. 120.5–121.0°. The benzoic acid from pure 2-phenylethane-1-C^{14} (above) was completely inactive.

Oxidation of 3-Phenylpropionaldehyde-2-C^{14}.—The aldehyde (3.0 g.) was oxidized by potassium permanganate (18.5 g.) in a basic solution (see above), and the benzoic acid (1.4 g., 42% yield, m.p. 120–121°) isolated and purified using the same procedure as described above. The benzoic acid was completely inactive.

Decarbonylation of 3-Phenylpropionaldehyde-2-C^{14}.—A one molar solution of 3-phenylpropionaldehyde-2-C^{14} (25.0 g., 0.0186 mole) in *o*-dichlorobenzene (160 ml., freshly distilled, Eastman reagent grade) which contained thiophenol (0.5 g., 2.5 mole % of the aldehyde; some of the decarbonylation reaction were run without thiophenol) and di-*t*-butyl peroxide (4.1 g., 0.028 mole; 15 mole % of the aldehyde) was placed in a flask. A Tygon tube from the top of the condenser was connected to an ice trap and then to a gas holder in which the gas evolved from the reaction was collected by the displacement of brine.

The solution was heated to the desired temperature (145 to 170°, see Table I) rapidly so that only 5 to 10% of the total gas evolved was at a lower temperature. The temperature of each run was maintained within a 5 degree range. After the gas evolution had subsided, another portion of di-*t*-butyl peroxide (4.1 g., 0.028 mole) was added and the reaction continued.

After gas evolution had ceased, gas samples were analyzed on the mass spectrometer and also on a 25-ft. gas chromatography column (30% dimethylsulfolane on firebrick) to determine the amount of carbon monoxide released and consequently the percentage of the aldehyde decomposed. The *o*-dichlorobenzene solution was washed several times with 20% sodium hydroxide solution, then water, and finally dried over anhydrous calcium chloride. The ethylbenzene-C^{14} resulting from the decarbonylation was recovered by fractionally distilling this solution through a 24-inch column packed with metal helices. A second distillation through a spinning band column gave ethylbenzene-C^{14} (b.p. 136.0–136.3°, $n^{20}\text{D}$ 1.4940) in yields of 51 to 77% of that anticipated frm the carbon monoxide evolution. The yields of carbon monoxide ranged from 69 to 76% of theoretical (see Table I). The ethylbenzene-C^{14} in each case was shown to be more than 98% pure by gas chromatography.

A portion of the ethylbenzene-C^{14} was oxidized to benzoic acid by the procedure described previously and the C^{14} content for both the benzoic acid and ethylbenzene-C^{14} measured (see Table I).

Benzyl Mercaptan-S-*t*.—Anhydrous ethanol (10 ml.), benzyl mercaptan (100 g., 0.81 mole; Eastman white label) and tritium labeled water (0.100 ml., 0.8 mc.) were mixed,

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(18) The actual exchange of the ethylbenzene-*t* and *n*-propylbenzene was probably higher than that indicated by the tritium activity measurements because of an isotope effect involved in the reaction of an arylalkyl radical with benzyl mercaptan-S-*t* (equation 9). However, the conclusion that the presence of ethylbenzene-α-*t* concentration was due to exchange and not to 1,2-hydrogen atom migration is unaltered.

(19) It has been brought to our attention that J. C. Kauer (Ph.D. Thesis, University of Illinois, 1955) has decarbonylated 3-deuterio-3-*p*-anisyl-3-phenylpropionaldehyde and recovered 1-deuterio-1-*p*-anisyl-1-phenylethane as the only hydrocarbon product, indicating that no aryl or deuterium rearrangement took place.

(20) Melting points and boiling points have not been corrected.

(21) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

(22) H. Cohen, *J. Chem. Soc.*, 432 (1935).

allowed to stand overnight and distilled giving a near quantitative recovery of benzyl mercaptan-S-*t*, b.p. 197.1–198.8° (271,000 d.p.m./mmole).

Decarboxylation of 3-Phenylpropionaldehyde in the Presence of Benzyl Mercaptan-S-*t* and *n*-Propylbenzene.—In a flask were placed freshly distilled Eastman 3-phenylpropionaldehyde (35.0 g., 0.261 mole, b.p. 101.5–102.4° at 13 mm.), *o*-dichlorobenzene (224 ml., b.p. 180–181°) *n*-propylbenzene (16.0 g., 0.133 mole, b.p. 158.8–159.3°), di-*t*-butyl peroxide (4.1 g., 0.028 mole) and benzyl mercaptan-S-*t* (3.0 g., 0.024 mole) making a one molar solution of the aldehyde. The aldehyde was decomposed (140–155°) until 26.4% of the theoretical amount of carbon monoxide had been liberated, after which 18.0 g. of active ethylbenzene was added to ensure that there would be enough for purification and subsequent degradation. Using the procedure above, ethylbenzene-*t* (16.2 g., 64.6%), b.p. 136.4–136.8°, and the *n*-propylbenzene (9.8 g., 61.3% recovery), b.p. 159.3–159.5°, were obtained after distilling twice. Gas chromatography analysis showed the ethylbenzene-*t* was 99.8% pure and that the *n*-propylbenzene was 99.9% pure. The tritium activities of these samples were measured and are given in Table II.

Bromination of Ethylbenzene-*t*.—The light (ultraviolet)-catalyzed bromination of ethylbenzene-*t* (11.5025 g., 0.1084 mole; resulting from the decarbonylation above) in the α-position was carried out at reflux temperature in carbon tetrachloride (130 ml.) with a stoichiometric amount of N-bromosuccinimide (19.5750 g., 0.1084 gram atom of active bromine as determined by iodometric analysis; freshly recrystallized from boiling water and dried over phosphorus pentoxide). The succinimide produced was collected by filtration, repeatedly washed with cold carbon tetrachloride and recrystallized twice from hot toluene. Before the tritium activity was measured, the succinimide was shown to contain no bromine.

Radioactivity Measurements.[23]—The C^{14} and H^3 activities of the compounds were determined by the liquid scintillation method[24,25] employing toluene as the organic solvent for all the compounds except succinimide which was dissolved in a solvent consisting of equal amounts of 1,4-dioxane and toluene. In general, counting efficiencies were about 75% for C^{14} and 25% for H^3. All net counting rates were converted to disintegrations per minute (d.p.m.) by measurement of the exact counting efficiencies with calibrated H^3 and C^{14} solutions.

Acknowledgment.—The author wishes to thank Drs. V. P. Guinn, J. H. Raley and M. M. Wald for valuable discussions during the course of this work. Dr. V. P. Guinn also furnished the radioactivity measurements.

(23) All of the radioactivity measurements were carried out by Dr. V. P. Guinn of the Shell Development Co.

(24) V. P. Guinn, paper presented at Northwestern University Conference on Liquid Scintillation Counting, August, 1957, in press, Pergamon Press.

(25) C. D. Wagner and V. P. Guinn, *Nucleonics*, **13** (10), 56 (1955).

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

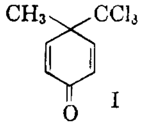
A New Synthesis of 3,4-Dichlorocoumarins[1]

BY MELVIN S. NEWMAN AND SIDNEY SCHIFF

RECEIVED NOVEMBER 1, 1958

A new synthesis of 3,4-dichlorocoumarins, which involves the aluminum chloride-catalyzed reaction of perchloropropylene with phenols, is described. The 4-chloro group in these coumarins is reactive and easily displaced by several nucleophilic reagents.

The reaction of *p*-cresol with carbon tetrachloride under the influence of aluminum chloride affords 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (I).[2,3]



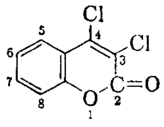
I

In seeking to extend the generality of this reaction, the condensations of cresol with benzotrichloride[4] and substituted benzotrichlorides[5] were studied. Although these reactions led to the formation of several new substances, no compounds analogous to I were isolated.

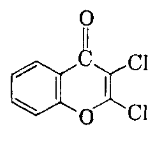
We now show that the condensation of *p*-cresol and of other phenols with hexachloropropene in the presence of aluminum chloride yields 3,4-dichlorocoumarins. The scope and limitations of this new reaction as well as the reactions of the 3,4-dichlorocoumarins form the subject matter of this paper.

In our first experiments, hexachloropropylene was allowed to react with the salt formed by treating *p*-cresol with aluminum chloride in carbon disulfide. After hydrolysis a solid was isolated from which a colorless compound, $C_{10}H_8O_2Cl_2$, II, was obtained on vacuum sublimation.[6] On oxidation of II with chromic acid an acid, $C_{10}H_4O_4Cl_2$, III, was obtained. This suggested that a methyl group had been oxidized to a carboxyl.[6] After it was found that hexachloropropene reacted with phenol to give a compound, $C_9H_4O_2Cl_2$, which appeared analogous to II, all further work was carried out with the compound obtained from phenol.

Two structures were believed likely: 3,4-dichlorocoumarin (IV) and 2,3-dichlorochromone (V).



IV



V

A decision in favor of structure IV was reached when 3-chloro-4-hydroxycoumarin[7] was converted into a compound identical with ours by treatment with phosphorus oxychloride in pyridine. This conversion was not conclusive by itself as the

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(1) Taken from the Ph.D. Thesis of S. Schiff, O.S.U., 1958.

(2) T. Zincke and R. Suhl, *Ber.*, **39**, 4148 (1906).

(3) M. S. Newman and A. G. Pinkus, *J. Org. Chem.*, **19**, 978 (1954).

(4) M. S. Newman and A. G. Pinkus, *ibid.*, **19**, 985 (1954).

(5) M. S. Newman and A. G. Pinkus, *ibid.*, **19**, 996 (1954).

(6) This compound was first obtained by A. G. Pinkus who carried out preliminary experiments but did not prove the structure.

(7) F. Arndt, L. Loewe, R. Ün and E. Ayça, *Ber.*, **84**, 319 (1951).