In essence, these data show that in each of these reactions the conversion of olefin to alcohol is accompanied by a decrease in entropy on the order of 20 cal. deg.$^{-1}$ mole^{-1}, but, according to expectations the ordinary aliphatic olefins have transition states whose formation from olefin results in little change in entropy. The α,β-unsaturated aldehydes, on the other hand, have transition states which are formed with a decrease in entropy even slightly greater than that for the olefin to alcohol conversion.

The complete accord between the entropies of activation from the absolute rate theory and the Hammett theory regarding the hydration mechanisms indicates that both are powerful tools for the investigation of reaction mechanisms.

Acknowledgment.—The author appreciates the helpful comments of Drs. F. A. Long, Victor Gold, N. C. Deno and L. P. Hammett.

Experimental

The experimental method was the same as previously reported (procedure B).[2] In every case plots of log ($P - P^e$) *vs.* time gave straight lines over the entire region of the reaction studied (60 to 91% completion) and of the same high precision previously obtained. The rate constants, k_p, for 0.0909 and 0.973 *m* HNO_3 were obtained from the previous data.[2] In the other cases values of k_p are average values obtained by equation (5) of reference 2 from at least two experiments conducted at the indicated acidity. A value of h of 6×10^{-3} mole l.$^{-1}$ atm.$^{-1}$ was used in each case to calculate k_p. The pair of experiments (at given acidity) were carried out at appreciably different r values (r/RT = 0.08 to 0.125) but of such a magnitude that an error of 50% in h would introduce an error of no more than 3% in k_p. Shaking rates of 333 to 400 r.p.m. were used (the latter at the higher acidities). The temperature was controlled to 25.00 ± 0.01°.

In every case but for 5.04 *m* HNO_3, the calculated values of k_p for the two experiments agreed to within 2%, and the internal consistency with equation (5) was as good as the accuracy warrants. In the exceptional case, four experiments were performed and the maximum deviation from the average value of k_p was 7%. No systematic deviation of the k_p values with r was obtained, indicating (in view of the excellent nature of plots of log ($P - P^e$) *vs.* time) that the reaction rate is so fast in this case ($t_{1/2}$ 6 to 10 minutes) as to approach the limit of accuracy of the experimental method. In view of these results, the value of k_p given for 5.04 *m* HNO_3 should be accurate to 10%, whereas the other values should not be in error by more than 5% (probably less in most cases).

Experiments were also performed in the 1.242, 3.111 and 6.22 *m* sulfuric acid solutions. In the former case, the values of k_p calculated as above from two experiments agreed within 5%. The average value is reported in Table I. In the latter two cases, the values of k_p calculated from experiments carried out at appreciably different r values differed by as much as 30%. Four experiments were performed in 3.111 *m* sulfuric acid, and the calculated values of k_p showed a regular decrease with increasing r. A more marked trend in the same direction was shown by k_p values calculated from two experiments in 6.22 *m* acid. The results in 3.111 and 6.22 *m* acid are not listed in Table I since the data indicate that equation (5) does not hold under these conditions. No reason can be given for these results, and the system was not further investigated. The crude values of k_p obtained in these two cases are markedly less than the corresponding values in nitric acid solution at equivalent h_0.

STATE COLLEGE, PENNA.

[CONTRIBUTION 1097 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Copper-catalyzed Decomposition of Diazoketones[1]

BY PETER YATES[2]

RECEIVED APRIL 18, 1952

The reaction of α-diazoketones with alcohols in the presence of copper has been shown to occur without rearrangement to give α-alkoxyketones. The reaction of α-diazoacetophenone with phenol, thiophenol, aniline and piperidine has also been shown to yield the analogous unrearranged products: in the reaction with phenol, 2-phenylbenzofuran was obtained as a second product. It is suggested that these reactions proceed with the intermediate formation, by the interaction of the diazoketone and copper, of the moiety, RCÖCH, which then reacts with the active hydrogen compound.

Arndt and Eistert[3] state that silver, copper or platinum may be used as catalysts for the decomposition with rearrangement of diazoketones, *i.e.*, for the Wolff rearrangement. Subsequent general discussions[4,5] of the Arndt–Eistert reaction have reiterated that copper may be used in place of the conventional silver oxide. The original literature, however, reveals very few instances of the use of copper. Arndt and Eistert[3] treated diazomethyl α-naphthyl ketone with aqueous ammonia in the presence of copper at 100° and obtained α-naphthylacetamide in 20% yield, whereas by the use of ammoniacal silver nitrate at 100° the amide was obtained in 85% yield. The only other reference by these authors to the use of copper is to its action on 2-diazoacetyl-1-nitroanthracene in acetic acid solution, when the evolution of nitrogen and the formation of a red color was observed but no product was isolated. Reichstein and Morsman[6] observed that the action of copper on methyl α-diazothienonylacetate in methanol at 140–150° gave the methyl ester of thienylmalonic acid together with another unidentified product; the yield was unspecified. *Thus it may be seen that in the few cases where copper has been used in the Wolff rearrangement, either the yields have been abnormally low or the conditions have been abnormally forced.*

In a search for a catalyst more efficacious than silver oxide the decomposition of 1-diazo-2-nonadecanone[7] in ethanolic solution at 65–70° in the

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(1) From a dissertation presented to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1951.

(2) Socony-Vacuum Company Fellow, Yale University, 1949–1950.

(3) F. Arndt and B. Eistert, *Ber.*, **68**, 203 (1935).

(4) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

(5) B. Eistert, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 513.

(6) T. Reichstein and H. J. Morsman, *Helv. Chim. Acta*, **17**, 1119 (1934).

(7) *Cf.* F. A. Vandenheuvel and P. Yates, *Can. J. Research*, **B28**, 556 (1950).

presence of copper bronze (*i.e.*, very finely divided copper) has been investigated. It was found, however, that, although the rate of decomposition of 1-diazo-2-nonadecanone, as judged by the rate of evolution of nitrogen, was considerably increased by the use of copper, the product obtained was not ethyl nonadecanoate but 1-ethoxy-2-nonadecanone

$$C_{17}H_{35}COCHN_2 + C_2H_5OH \xrightarrow{Cu} C_{17}H_{35}COCH_2OC_2H_5 + N_2 \quad (1)$$

In this case the diazoketone has reacted with an alcohol *without rearrangement.* The generality of this reaction has been demonstrated by the preparation of α-methoxy-, α-ethoxy-, α-(*t*-butoxy)- and α-(1-hexoxy)-acetophenone by the copper-catalyzed decomposition of α-diazoacetophenone in hot methanol, ethanol, *t*-butyl alcohol and hexyl alcohol, respectively. The alkoxy-ketones were identified by the preparation of their 2,4-dinitrophenylhydrazones and semicarbazones and, in the case of α-methoxyacetophenone, direct comparison with an authentic sample. Further, a diazoketone derived from diazoethane, α-diazopropiophenone, was shown to give the corresponding α-ethoxyketone[8] with copper in ethanol.

This appears to be the first report of the formation of unrearranged products by the action of alcohols with diazoketones in the presence of copper. Casanova and Reichstein[9] have recently reported an analogous decomposition without rearrangement of certain steroidal diazoketones in the presence of cupric oxide. These workers, however, were able to isolate only the rearranged product, methyl phenylacetate, by the action of cupric oxide on α-diazoacetophenone in methanol; whereas in the present investigation, using metallic copper, the only product isolated was α-methoxyacetophenone. An analogous homogeneous reaction has also recently been reported by Newman and Beal[10] who used boron trifluoride as catalyst; since the yields of alkoxy-ketones in the homogeneous reaction are of the order 70–80% this would appear to be a better preparative method than the copper-catalyzed reaction where the yields so far obtained have been of the order 45–55%.

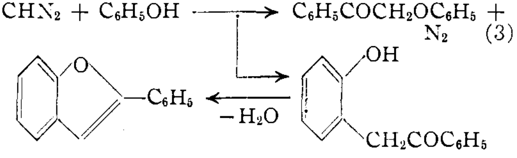
Once it had been established that the reaction of diazoketones with alcohols in the presence of copper followed the reaction path

$$RCOCHN_2 + R'OH \xrightarrow{Cu} RCOCH_2OR' + N_2 \quad (2)$$

it became of interest to investigate the copper-catalyzed decomposition of α-diazoacetophenone in the presence of phenol, thiophenol, aniline and piperidine.

A solution of α-diazoacetophenone in benzene was added to a suspension of copper bronze[11] in a benzene solution of phenol at 65–70°. The product was separated into two fractions by extraction with aqueous base. The non-acidic fraction gave a 63% yield of α-phenoxyacetophenone, in conformance with the formulation (2). Acidification of the basic extract gave a product which would not redissolve in aqueous base. This second product was shown to be 2-phenylbenzofuran and was obtained in 26% yield. Clearly, the original acidic product was α-(*o*-hydroxyphenyl)-acetophenone which underwent cyclodehydration in the process of isolation[12]

$$C_6H_5COCHN_2 + C_6H_5OH \xrightarrow{Cu} C_6H_5COCH_2OC_6H_5 + N_2 \quad (3)$$



The copper-catalyzed reaction of α-diazoacetophenone with thiophenol was carried out in ethanol solution, yielding mainly α-phenylmercaptoacetophenone (67%). There was also isolated some diphenyl disulfide[13]

$$C_6H_5COCHN_2 + C_6H_5SH \xrightarrow{Cu} C_6H_5COCH_2SC_6H_5 + C_6H_5SSC_6H_5 + N_2 \quad (4)$$

By the action of copper on an ethanolic solution of α-diazoacetophenone and excess aniline at 60–70° and extraction of the crude product with boiling ethanol, α-anilinoacetophenone was obtained in 33% yield; the small residue insoluble in boiling ethanol was found to be the mono-anil of phenylglyoxal[14]

$$C_6H_5COCHN_2 + C_6H_5NH_2 \xrightarrow{Cu} C_6H_5COCH_2NHC_6H_5 + C_6H_5COCH{=}NC_6H_5 + N_2 \quad (5)$$

Finally, it was found that under similar conditions piperidine reacts with α-diazoacetophenone to give two products, α-(1-piperidyl)-acetophenone and dibenzoylethane[15]

$$C_6H_5COCHN_2 + HN(CH_2)_5 \xrightarrow{Cu} C_6H_5COCH_2N(CH_2)_5 + C_6H_5COCH_2CH_2COC_6H_5 + N_2 \quad (6)$$

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(8) It was of interest to find that both a simple 2,4-dinitrophenylhydrazone and a 2,4-dinitrophenylosazone could be obtained from α-ethoxypropiophenone. H. Adkins and A. G. Rossow, THIS JOURNAL, **71**, 3836 (1949), have reported the analogous formation of a 2,4-dinitrophenylosazone from 2-ethoxycyclohexanone; a similar observation in the case of 3-methoxy-2-butanone was made by J. G. Aston, J. T. Clarke, K. A. Burgess and R. B. Greenburg, *ibid.*, **64**, 300 (1942).

(9) R. Casanova and T. Reichstein, *Helv. Chim. Acta*, **33**, 417 (1950).

(10) M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5161 (1950).

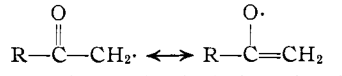
(11) The only product obtained from the reaction of copper and α-diazoacetophenone in the presence of benzene alone was *trans*-1,2-dibenzoylethylene; *cf.* C. Grundmann and H. Trischmann, *Ann.*, **536**, 29 (1938).

(12) *Cf.* W. Dilthey and F. Quint, *J. prakt. Chem.*, **131**, 3 (1931), who obtained only 2-phenylbenzofuran by the hydrolysis of the benzoyl derivative of α-(*o*-hydroxyphenyl)-acetophenone.

(13) *Cf.* the preparation of diphenyl disulfide by bubbling air through thiophenol, W. Steinkopf and S. Muller, *Ber.*, **56**, 1929 (1923).

(14) This must be produced by air oxidation of α-anilinoacetophenone, for an ethanolic solution of this compound was found slowly to deposit the anil on standing; *cf.* the formation of benzil monoanil from α-anilino-α-phenylacetophenone by the action of oxygen, P. L. Julian, E. W. Meyer, A. Magnani and W. Cole, THIS JOURNAL, **67**, 1203 (1945).

(15) *Cf.* A. F. Crowther, F. G. Mann and D. Purdie, *J. Chem. Soc.*, 58 (1943), who report the formation of 1,2-dibenzoylethane by the thermal fission of α-(1-piperidyl)-acetophenone. This reaction probably involves the intermediate formation of the phenacyl radical



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2\cdot \longleftrightarrow R{-}\overset{\overset{\displaystyle O\cdot}{|}}{C}{=}CH_2$$

which must also be an intermediate in the formation of 1,2-dibenzoylethane by the action of sulfur on acetophenone (T. W. Jezierski, *Roczniki Chem.*, **14**, 216 (1934); *C. A.*, **29**, 2161 (1935)).

Discussion

In every case investigated using copper as catalyst no rearranged product was isolated. Equations (2)–(6) may be combined in the form of equation (7) which represents the formation of the chief product in each instance

$$RCOCHN_2 + R'H \longrightarrow RCOCH_2R' + N_2 \qquad (7)$$

Although a more comprehensive study of the reaction is required in order to formulate an unambiguous mechanism, the following scheme is advanced at this time as the most reasonable hypothesis compatible with the observed facts and as a basis for further work

$$RCO\ddot{C}HN_2 \xrightarrow{Cu} RCOCH + N_2 \qquad (8)$$

$$RCO\ddot{C}H + R'H \longrightarrow RCOCH_2R' \qquad (9)$$

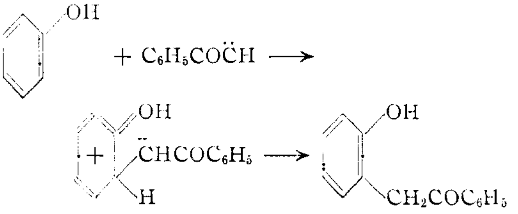
The action of copper in (8) is interpretable in terms of the ready availability of its valence electrons[16]; the entity $RCO\ddot{C}H$[16a] may well remain bound to the copper surface with the valence electrons of the copper completing the octet of the methine carbon. The subsequent reaction of $RCO\ddot{C}H$ (or of the $RCO\ddot{C}H$-copper complex) as in (9) probably involves an attack by the unshared pair of electrons on oxygen, nitrogen or sulfur at the electron-deficient methine carbon[17] followed by a prototropic shift, *e.g.*

$$C_6H_5CO\ddot{C}H + C_6H_5NH_2 \longrightarrow C_6H_5CO\overset{-}{C}H\overset{+}{N}_2HC_6H_5 \qquad (9a)$$

$$C_6H_5CO\overset{-}{C}H\overset{+}{N}H_2C_6H_5 \longrightarrow C_6H_5COCH_2NHC_6H_5 \qquad (10)$$

In an inert solvent, such as benzene or petroleum ether, the formation of an enedione[11] may be considered as occurring by either the union of two adjacent $RCO\ddot{C}H$ moieties at the surface of the copper[18] or the interaction of $RCO\ddot{C}H$ with a molecule of diazoketone.

Furthermore, the formation of 2-phenylbenzofuran in addition to α-phenoxyacetophenone by the reaction of α-diazoacetophenone with phenol is readily explicable in terms of this reaction scheme. Thus the attack by $RCO\ddot{C}H$ at the oxygen atom would be slower than in the case of the aliphatic alcohols since it is less basic[19] and reaction at another site could become significant. The strongly electrophilic $RCO\ddot{C}H$ could attack the benzene ring in the activated position ortho to the hydroxyl group in a manner entirely analogous to the action of Br^+ in aromatic bromination[20]; the intermediate so formed would then be converted by a prototropic shift to α-(*o*-hydroxyphenyl)-acetophenone and this transformed to 2-phenylbenzofuran as discussed above



(11)

It has been frequently suggested[4] that the Wolff rearrangement proceeds by the loss of nitrogen from a diazoketone with the formation of a short-lived radical, RCOCH<, which rearranges to a ketene. It appears from our results, however, that a ketene is not necessarily formed by the loss of nitrogen from a diazoketone and that some fuller explanation of this rearrangement must be sought.[21]

Experimental[24]

Action of Copper on 1-Diazo-2-nonadecanone in Ethanol. 1-Ethoxy-2-nonadecanone.—1-Diazo-2-nonadecanone[7] (5 g.) was dissolved in absolute ethanol (50 ml.) heated at 65–70°. The solution was treated with copper bronze[25] in small portions at a time with mechanical stirring until no further gas evolution occurred on adding a fresh portion of copper. The mixture was filtered free of copper and evaporated to small bulk; on cooling at 0°, 4.6 g. of yellow solid was deposited. This crude product was twice recrystallized from 95% ethanol with treatment with charcoal and gave a white solid, m.p. 54–55°; yield 3.6 g. (68%). For analysis a sample was recrystallized twice more from 95% ethanol, then three times from acetone giving white prisms, m.p. 56.5°.

Anal. Calcd. for $C_{21}H_{42}O_2$: C, 77.24; H, 12.97; OC_2H_5, 13.8. Found: C, 77.37; H, 13.08; OC_2H_5, 13.9.

The 2,4-dinitrophenylhydrazone[26] was purified by chromatography on silica with 95% petroleum ether–5% ether as eluent followed by two recrystallizations from absolute ethanol: yellow, m.p. 78.5–79.5°.

Anal. Calcd. for $C_{27}H_{46}O_5N_4$: N, 11.06. Found: N, 11.19.

The identity of the 1-ethoxy-2-nonadecanone was confirmed by its conversion to **2-nonadecanone**: 1 g. of the product was boiled under reflux with hydriodic acid (10 ml., d. 1.73) and glacial acetic acid (10 ml.) for two hours. The

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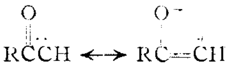
(16) *Cf.* W. A. Waters, *J. Chem. Soc.*, 266 (1942), where the catalytic effect of copper in the Gattermann reaction is interpreted in similar terms.

(16a) Such an entity would be stabilized by resonance:



$$R\overset{\overset{O}{\|}}{C}\ddot{C}H \longleftrightarrow R\overset{\overset{O^-}{|}}{C}{=}\dot{C}H$$

provided that the unshared electrons on the methine carbon are paired. This is probable by analogy with the case of methylene, CH_2:, *cf.* K. J. Laidler and E. J. Casey, *J. Chem. Phys.*, **17**, 213 (1949).

(17) The preferential reaction of the diazoketone with amine when both ethanol and amines are present in the reaction mixture, *i.e.*, with the more basic reactant, indicates that attack on $RCO\ddot{C}H$ is nucleophilic. The qualitative observation that the reaction of diazoketone proceeds much faster with piperidine than with aniline is also in conformance with this view.

(18) The formation of the *trans* product being due to a preferred orientation of the $RCO\ddot{C}H$ moieties on the copper surface such that the RCO groups are as far apart as possible.

(19) It may well be in the case of phenol (and thiophenol) that the reaction proceeds in part by an acid-catalyzed route, similar to that of the reactions of diazo compounds with carboxylic acids: *cf.* J. D. Roberts, W. Watanabe and R. E. McMahon, THIS JOURNAL, **73**, 760 (1951). This, however, need not affect the fate of the $RCO\ddot{C}H$ entity formed in the copper-catalyzed reaction.

(20) Alternatively, a norcaradiene type intermediate with subsequent rearrangement may be postulated; *cf.* W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950).

(21) A survey of the conditions normally used for the Wolff rearrangement reveals that a base is always present, *e.g.*, silver oxide, cupric oxide,[9] aniline,[1] isoquinoline,[22] triethylamine,[23] and lends support to the original suggestion of Arndt and Eistert[3] that the rearrangement is base-catalyzed.

(22) A. L. Wilds and A. L. Meader, *J. Org. Chem.*, **13**, 763 (1948).

(23) M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5163 (1950).

(24) All melting points are corrected.

(25) The copper bronze used throughout the present work was Kahlbaum, "Naturkupfer C" (*cf.* F. Ullmann, *Ber.*, **29**, 1878 (1896)).

(26) All 2,4-dinitrophenylhydrazones were prepared by the method of R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., Third Edition, 1948, p. 171.

mixture was cooled, depositing the crude product as a brown solid (1.0 g.); recrystallization from absolute ethanol with charcoal treatment gave a white crystalline solid, m.p. 49–54°. This was taken up in benzene and chromatographed on an alumina column (20 × 1.2 cm., packed in benzene), using benzene as eluent; arbitrary cuts of 15–20 ml. were taken. The first two cuts containing eluted material on removal of solvent gave white prisms, m.p. 51–55°; subsequent cuts gave white leaflets, m.p. 55–56.5,[27] undepressed by admixture with a sample of 2-nonadecanone obtained by the reduction of 1-diazo-2-nonadecanone with hydriodic acid.[28]

A qualitative comparison of the rates of decomposition of 1-diazo-2-nonadecanone in ethanol with silver oxide, copper and cupric oxide was made by adding 0.5 g. of each to solutions of 1-diazo-2-nonadecanone (0.5 g.) in ethanol (5 ml.)

TABLE I

Catalyst	Evolution of nitrogen	Product
Silver oxide	Slow: complete in 2.0 hr.	$C_{18}H_{37}COOEt$
Copper	Immediate and rapid, complete in 0.25 hr.	$C_{17}H_{35}COCH_2OEt$
Cupric oxide	Initially slow, gradually becoming vigorous, complete in 0.7 hr.	$C_{17}H_{35}COCH_2OEt$

Action of Copper on α-Diazoacetophenone in Methanol. α-Methoxyacetophenone.—α-Diazoacetophenone[29] (6 g.) was dissolved in methanol (60 ml.) at 50–55° and treated with copper bronze (1 g.) as above. There was a vigorous evolution of nitrogen and the reaction solution rapidly assumed a dark red color. It was filtered free of copper and distilled under reduced pressure from the steam-bath to remove excess methanol. Distillation of the residual liquid at 18 mm. pressure gave one fraction only, a pale yellow liquid, b.p. 122–123° (18 mm.), $n^{20}D$ 1.5340, λ_{max} (ethanol) 244 mμ (log ε 4.03) and 280 mμ (log ε 3.02); yield 3.4 g. (55%). This was shown to be α-methoxyacetophenone by the identity of its physical properties with those of an authentic sample.[30]

The semicarbazone[31] was obtained after recrystallization from 25% aqueous ethanol and from 95% ethanol as a white crystalline solid, m.p. and mixed m.p. 127.5–128.5°.[32]

The 2,4-dinitrophenylhydrazone was prepared and purified by chromatography on alumina with benzene as solvent and eluent followed by two recrystallizations from ethyl acetate–ethanol: orange-red, hexagonal prisms, m.p. and mixed m.p. 192–194°.

Anal. Calcd. for $C_{15}H_{14}O_5N_4$: N, 16.96. Found: N, 17.01.

Action of Copper on α-Diazoacetophenone in Ethanol. α-Ethoxyacetophenone.—Using the same procedure as for the reaction in methanol a 60% yield of α-ethoxyacetophenone was obtained, b.p. 125–127° (14.5 mm.).

The semicarbazone was purified by four recrystallizations from 20% aqueous ethanol and was obtained as white, feathery needles, m.p. 126.5–127°.[33]

The 2,4-dinitrophenylhydrazone was purified by chromatography on silica followed by three recrystallizations from 95% ethanol: short, orange rods, m.p. 149.8–150.3°.

Anal. Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.35; H, 4.67; N, 16.27. Found: C, 55.36; H, 4.56; N, 16.10.

Action of Copper on α-Diazoacetophenone in Presence of Hexyl Alcohol. α-(1-Hexoxy)-acetophenone.—α-Diazoacetophenone (5 g.) and hexyl alcohol (redistilled, b.p. 156–157°) were dissolved in dioxane (40 ml.). The solution was heated at 70–80° and treated with copper bronze as before. Distillation of the product did not give a sharp boiling fraction but a distillate boiling over the range 120–150° (5 mm.). The crude product was thus obtained as a yellow mobile liquid in 20% yield. This product was not further purified but identified by conversion to the two following derivatives in good yield.

The semicarbazone after two recrystallizations from 50% aqueous ethanol and two more from 95% ethanol was obtained as white prisms, m.p. 104–105°.

Anal. Calcd. for $C_{15}H_{23}O_2N_3$: C, 64.96; H, 8.36; N, 15.15. Found: C, 65.13; H, 8.49; N, 14.98.

The 2,4-dinitrophenylhydrazone purified by chromatography on alumina followed by four recrystallizations from a mixture of ethyl acetate and 95% ethanol was obtained as golden yellow needles, m.p. 124–125°.

Anal. Calcd. for $C_{20}H_{24}O_5N_4$: C, 60.00; H, 6.04; N, 14.00. Found: C, 60.06; H, 6.05; N, 13.82.

Action of Copper on α-Diazoacetophenone in *t*-Butyl Alcohol. α-(*t*-Butoxy)-acetophenone.—*t*-Butyl alcohol (25 ml.) was heated at 60° and a little copper bronze was added during mechanical stirring. A small portion of a solution of α-diazoacetophenone (5 g.) in *t*-butyl alcohol (35 ml.) was then added. After ten minutes stirring a vigorous gas evolution set in and the temperature rose. The remainder of the diazoketone solution was dropped in at such a rate that a steady gas evolution was maintained and the temperature remained at 55–60°. During this addition further small portions of copper bronze were added from time to time: the total weight of copper used was 0.75 g. Finally the mixture was heated at 65–70° for 30 minutes. The product was worked up as before giving α-(*t*-butoxy)-acetophenone as a pale yellow liquid, b.p. 116–118° (7 mm.), $n^{25}D$ 1.5156, in 30% yield. This was identified by the following derivatives obtained in good yield.

The semicarbazone was purified by two recrystallizations from 20% aqueous ethanol; fine, white needles, m.p. 126–127.5°.

Anal. Calcd. for $C_{13}H_{19}O_2N_3$: C, 62.62; H, 7.68; N, 16.86. Found: C, 62.69; H, 7.17; N, 16.74.

The 2,4-dinitrophenylhydrazone was twice recrystallized from a mixture of ethyl acetate and 95% ethanol; fine, orange needles, m.p. 183–185° (Newman and Beal[10] give m.p. 185–187°).

Action of Copper on α-Diazopropiophenone in Ethanol. α-Ethoxypropiophenone.—α-Diazopropiophenone in ethanol at 60–70° was treated with copper bronze and the product worked up as before; the crude product was obtained in 52% yield. Redistillation gave the α-ethoxypropiophenone as a pale yellow liquid, b.p. 97–98° (5 mm.), $n^{25}D$ 1.5193.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.93. Found: C, 73.60; H, 7.64.

The 2,4-dinitrophenylhydrazone was purified by chromatography on alumina followed by two recrystallizations from ethyl acetate–95% ethanol: orange prisms, m.p. 128–129°.

Anal. Calcd. for $C_{17}H_{18}O_5N_4$: C, 56.98; H, 5.06; N, 15.64. Found: C, 56.72; H, 4.93; N, 15.41.

When the crude product obtained by precipitation with 2,4-dinitrophenylhydrazine sulfate was not chromatographed but directly crystallized from benzene and then twice from ethyl acetate–95% ethanol, methyl phenylglyoxal osazone was isolated as orange, microscopic rods, m.p. 155–156° (dec.)

Anal. Calcd. for $C_{21}H_{16}O_8N_8$: C, 49.61; H, 3.17; N, 22.04. Found: C, 49.45; H, 3.09; N, 21.80.

Action of Copper on α-Diazoacetophenone in the Presence of Phenol. α-Phenoxyacetophenone and 2-Phenylbenzofuran.—α-Diazoacetophenone (5 g.) was dissolved in benzene (50 ml.) and the solution was slowly added to a stirred suspension of copper bronze (1 g.) in a solution of phenol (8 g.) in benzene (50 ml.) heated at 65–70°. After addition of 10 ml. of the diazoketone solution a vigorous reaction ensued with rise in temperature to the boiling point. The remainder of the diazoketone solution was added at a rate such that the reaction mixture was kept boiling gently: after completion of the addition the mixture was heated at 65–70° for 15 minutes. The hot mixture was filtered and the filtrate cooled and extracted several times with 8% aqueous sodium hydroxide. The benzene layer was washed

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(27) W. B. Saville and G. Shearer, *J. Chem. Soc.*, 593 (1925), give m.p. 55.5–56° for 2-nonadecanone.

(28) *Cf.* M. L. Wolfrom and R. L. Brown, THIS JOURNAL, **65**, 1516 (1943).

(29) W. Bradley and R. Robinson, *J. Chem. Soc.*, 1310 (1928).

(30) R. B. Moffet and R. L. Shriner, *Org. Syntheses*, **21**, 79 (1941).

(31) All semicarbazones were prepared by the method of R. L. Shriner and R. C. Fuson, *cf.* ref. (26), p. 170.

(32) C. Dufraisse and R. Chaux, *Bull. soc. chim. France*, [4] **39**, 446 (1926), give m.p. 126–127°, but D. D. Pratt and R. Robinson, *J. Chem. Soc.*, 748 (1923), give m.p. 85°.

(33) M. Sommelet, *Bull. soc. chim. France*, [4] **1**, 390 (1907), gives m.p. 128°.

several times with water and dried; after removal of the benzene there was obtained a brown semi-solid product (4.6 g.). Crystallization from aqueous ethanol followed by two recrystallizations from methanol with charcoal treatment gave a white, micro-crystalline solid, m.p. 73–73.5°, showing no depression on admixture with authentic α-phenoxyacetophenone obtained by the action of phenacyl bromide on sodium phenate.[34]

The alkaline extracts and aqueous washings were combined and the whole was made slightly acid with hydrochloric acid: the buff colored precipitate formed was filtered off and washed with cold water to remove traces of phenol: yield 1.9 g. Two crystallizations from aqueous methanol followed by two from absolute methanol gave white leaflets, m.p. 120.8–121.2°, insoluble in 8% aqueous sodium hydroxide.

This product was identified as 2-phenylbenzofuran by its analysis, melting point,[35] coloration with concentrated sulfuric acid,[36] and ultraviolet absorption spectrum: λ_{max} (in alcohol) 224 mμ (log ε 3.96), 302 mμ (log ε 4.39) and 315 mμ (log ε 4.28).[37]

Action of Copper on α-Diazoacetophenone in Benzene. *trans*-1,2-Dibenzoylethylene.—α-Diazoacetophenone in benzene at 65–70° was treated with copper and worked up in the usual manner. After removal of solvent a sticky brown solid remained: three crystallizations of this product from ligroin gave lemon-yellow, foliated leaflets, m.p. 110–110.5°, undepressed on admixture with authentic *trans*-1,2-dibenzoylethylene,[11] yield 70%.

Action of Copper on α-Diazoacetophenone in the Presence of Thiophenol. α-Phenylmercaptoacetophenone.—α-Diazoacetophenone (5 g.) and thiophenol (10 ml., freshly distilled, b.p. 168–169°) were dissolved in absolute ethanol (50 ml.) at 70° and treated with copper bronze as above: after no further gas evolution occurred on the addition of a fresh portion of copper the mixture was stirred at 70–75° for seven hours. The copper was filtered off and the ethanol and most of the excess thiophenol was removed by distillation at the water pump. The residual liquid was taken up in ether and extracted several times with 8% aqueous sodium hydroxide to remove traces of thiophenol; the ethereal layer was washed twice with water and dried. On removal of the ether a brown mobile liquid (8 g.) remained. By chromatography of an aliquot portion (2.0 g.) of this product on alumina using ligroin–benzene eluents two compounds were isolated, each being obtained as white needles after two recrystallizations from absolute ethanol.

The compound first eluted (0.5 g.) had m.p. 60–61.5°, undepressed by admixture with authentic diphenyl disulfide[13]; it dissolved in concentrated sulfuric acid giving a violet coloration.[38]

The second product had m.p. 52.5–54°, undepressed by admixture with authentic α-phenylmercaptoacetophenone, obtained by the action of sodium thiophenate on phenacyl chloride.[39]

The oxime was obtained as colorless needles, m.p. 80–81°.[40]

The 2,4-dinitrophenylhydrazone was purified by chromatography on alumina with benzene followed by two crystallizations from ethyl acetate–95% ethanol: orange prisms, m.p. 149–150°.

Anal. Calcd. for $C_{20}H_{16}O_4N_4S$: C, 58.82; H, 3.95; N, 13.72; S, 7.85. Found: C, 58.96; H, 3.90; N, 13.82; S, 8.38.

The yield of α-phenylmercaptoacetophenone from α-diazoacetophenone was 67%.

Action of Copper on α-Diazoacetophenone in the Presence of Aniline. α-Anilinoacetophenone and Phenylglyoxal Mono-anil.—α-Diazoacetophenone (5 g.) and freshly distilled aniline (10 ml.) were dissolved in absolute ethanol (50 ml.) at 60–70° and the solution was treated with copper bronze. After an initial period of apparent inaction a vigorous reaction took place. The hot reaction mixture was filtered free of copper and on cooling deposited a pale yellow solid (2.55 g.), m.p. 90–155°. Removal of solvent from the mother liquor by distillation under reduced pressure gave a black tar: attempts to obtain further solid product from this were unsuccessful. The yellow solid was treated with 100 ml. of hot 95% ethanol: the bulk of the product went into solution but by filtration of the hot solution there was obtained 0.2 g. of deep yellow, insoluble residue, m.p. 150–160°. The filtrate was evaporated to small bulk in a stream of nitrogen and the crystalline product obtained on cooling was subjected to two recrystallizations from 95% ethanol giving very pale yellow needles, m.p. and mixed[41] m.p. 98–99°.

The N-benzoyl derivative was obtained after three recrystallizations from 95% ethanol as white needles, m.p. 156–157°, undepressed by admixture with the N-benzoyl derivative of authentic α-anilinoacetophenone, m.p. 156.5–157.5°.[42]

The deep yellow product insoluble in hot 95% ethanol was recrystallized three times from ethyl acetate when it gave golden yellow, micro-needles, m.p. 163–164° (dec.). A further 0.15 g. of this product was obtained by extracting the copper residues from the original reaction with benzene. The melting point was not depressed on admixture with phenylglyoxal mono-anil, m.p. 164–166° (dec.), obtained by heating phenylglyoxal hydrate (0.75 g.) and aniline (0.45 g.) in 95% ethanol (5 ml.) with a few drops of acetic acid on the steam-bath for 15 minutes dilution with a little water, cooling and crystallization of the solid separating from ethyl acetate.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30; N, 6.70. Found: C, 80.32; H, 5.59; N, 6.94.

There was evidence that phenylglyoxal mono-anil is formed from α-anilinoacetophenone by air oxidation since the second crop of the latter from the alcoholic mother liquor after standing in the air for two days had become almost completely insoluble in 95% ethanol and after one recrystallization from ethyl acetate gave pure phenylglyoxal mono-anil.

Action of Copper on α-Diazoacetophenone in the Presence of Piperidine. α-(1-Piperidyl)-acetophenone and 1,2-Dibenzoylethane.—Piperidine (15 ml.) was dissolved in absolute ethanol (35 ml.) and the solution was stirred with copper bronze (0.5 g.) at 45°. α-Diazoacetophenone (5.0 g.) dissolved in absolute ethanol (20 ml.) was added slowly. An extremely vigorous reaction set in and the rate of addition was adjusted to maintain the temperature at 50° without external heating. After addition was complete, a further small portion of copper was added but no further gas evolution occurred. The mixture was filtered free of copper and excess piperidine and alcohol were removed on the steam-bath under reduced pressure. The dark brown oil which remained was distilled at 2 mm. pressure but no sharp-boiling fractions could be obtained. Treatment of an aliquot of the fractions boiling from 115–150° (2 mm.) with methyl iodide followed by two recrystallizations from absolute ethanol afforded an 80% yield of colorless α-(1-piperidyl)-acetophenone methiodide, m.p. and mixed[43,44] m.p. 175–175.5° (dec.).

The hydrochloride was obtained as white leaflets, m.p. and mixed[45] m.p. 220–222° (dec.).

The fractions boiling from 150–190° (2 mm.), which partly solidified on cooling, were taken up in boiling absolute ethanol and the solution was cooled, when long, white needles were deposited; two recrystallizations from 95% ethanol gave 1,2-dibenzoylethane, m.p. 146.5–147°,[46] undepressed by admixture with authentic 1,2-dibenzoylethane obtained by the reduction of *trans*-1,2-dibenzoylethylene (see above) with sodium hydrosulfite.[47]

The failure to obtain a sharp-boiling fraction of α-(1-piperidyl)-acetophenone was probably due to the co-distillation of 1,2-dibenzoylethane since the latter was shown to be present in the fractions boiling from 115–150° (2 mm.) by the precipitation of some 1,2-dibenzoylethane 2,4-dinitro-

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(34) R. Mohlau, *Ber.*, **15**, 2497 (1882).

(35) S. von Kostanecki and J. Tambor, *ibid.*, **42**, 826 (1909), give m.p. 120–121°.

(36) *Cf.* R. Stoermer and M. Reuter, *ibid.*, **36**, 3981 (1903).

(37) *Cf.* C. Wiegand and E. Merkel, *Med. u. Chem.*, **4**, 585 (1942).

(38) *Cf.* W. Nekrassow and N. N. Melnikow, *Ber.*, **62**, 2093 (1929).

(39) L. M. Long, THIS JOURNAL, **68**, 2159 (1946).

(40) E. Winkler, *J. prakt. Chem.*, **159**, 115 (1941), gives m.p. 81–82°.

(41) A. Bischler, *Ber.*, **25**, 2865 (1892); M. Busch and G. Hefele, *J. prakt. Chem.*, [2] **83**, 431 (1911), give m.p. 98–99°.

(42) R. Mohlau, *Ber.*, **15**, 2471 (1882), gives m.p. 144–145°.

(43) H. H. van Ark, *Arch. Pharm.*, **238**, 330 (1900), gives m.p. 185°.

(44) P. Rabe, W. Schneider and F. Braasch, *Ber.*, **41**, 874 (1908).

(45) F. F. Blicke and E. S. Blake, THIS JOURNAL, **52**, 235 (1930), give m.p. 210–211°; N. H. Cromwell, *ibid.*, **63**, 837 (1941), gives m.p. 226–227°.

(46) S. Kapl and C. Paal, *Ber.*, **21**, 3056 (1888), give m.p. 144–145°.

(47) J. B. Conant and H. B. Cutter, THIS JOURNAL, **44**, 2654 (1922).

phenylhydrazone by the addition of 2,4-dinitrophenylhydrazine sulfate solution to ethanolic solutions of the fractions. After chromatography on alumina followed by two crystallizations from ethyl acetate–95% ethanol this was obtained as deep orange needles, m.p. 248.5–249° (dec.),[48] undepressed on admixture with an authentic sample.

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NEW HAVEN, CONN.

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[48] C. F. H. Allen, D. M. Young and M. R. Gilbert, *J. Org. Chem.*, **2**, 235 (1937), give m.p. 250° (dec.).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY AND FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Free Radical Rearrangements in the Decarbonylation of Aldehydes[1a]

BY DAVID Y. CURTIN[1b] AND MARVIN J. HURWITZ

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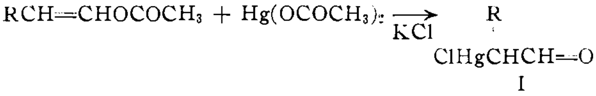
The peroxide-catalyzed free radical decarbonylation of aldehydes has been used to study the 1,2-rearrangements of four free radicals. β,β,β-Triphenylpropionaldehyde when heated with di-*t*-butyl peroxide has been found to yield only the rearranged hydrocarbon, 1,1,2-triphenylethane. α-Methyl-β,β,β-triphenylpropionaldehyde also gave only rearranged products, 1,1,2-triphenylpropane and 1,1,2-triphenyl-1-propene in approximately equal amounts. β-*p*-Anisyl-β-phenylpropionaldehyde gave predominately 1-*p*-anisyl-1-phenylethane with the carbon skeleton unrearranged. β,β-Diphenylbutyraldehyde yielded as the sole product 2,3-dibenzyl-2,3-diphenylbutane, dimer of the rearranged radical. The scope of the synthesis of aldehydes by the reaction of α-chloromercurialdehydes with alkyl chlorides has been extended and stannic chloride has been found to be an effective catalyst in at least one case where the reaction otherwise fails.

In the course of a general program of study of stereospecific rearrangements it was desirable to examine those involving free radical intermediates. It was first necessary to discover a rearrangement adaptable to this study. A part of this preliminary investigation is described here.

Only a few cases of carbon-to-carbon rearrangements in free radical reactions in solution have been reported thus far. Urry and Kharasch[2] have observed partial migration of the phenyl group of the 2-methyl-2-phenylpropyl (neophyl) radical in the reaction of neophyl chloride with phenylmagnesium bromide in the presence of cobaltous chloride. Of the yield of monomeric hydrocarbons obtained, approximately half was unrearranged (*t*-butylbenzene) while the other half consisted of saturated and unsaturated products from the rearranged (1-benzyl-1-methylethyl) radical. Similar results with the neophyl radical were obtained by Winstein and Seubold,[3] using a new method for the decarbonylation of aldehydes which had previously been carried out by irradiation.[4] β-Phenylisovaleraldehyde was treated with a peroxide catalyst, resulting in the evolution of carbon monoxide and a 70% yield of a 1:1 mixture of *t*-butylbenzene (unrearranged) and isobutylbenzene (migration of phenyl). Urry and Nicolaides[5] prepared the *p*-methylneophyl radical by both of the above methods and obtained rearranged products (again approximately 50% rearrangement). No migration of methyl groups was observed in the cobaltous chloride catalyzed reaction of 2,2-dimethylbutyl (neohexyl) chloride with ethylmagnesium bromide the only products being neohexane and bineohexane.

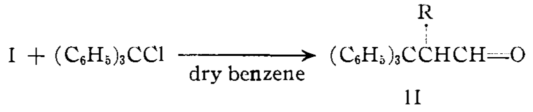
In this study, the peroxide-catalyzed decarbonylation of aldehydes was chosen as the most suitable reaction with which to study the carbon-to-carbon free radical rearrangement.

Synthesis of the Aldehydes Employed.—β,β,β-Triphenylpropionaldehyde (II, R = H) was synthesized by the method of Nesmeyanov, Lutsenko and Tumanova[6] by the treatment of trityl chloride with chloromercuriacetaldehyde (I, R = H) in dry benzene. (I, R = H) was readily prepared by the reaction of vinyl acetate with mercuric acetate and then potassium chloride.



$$\mathrm{RCH{=}CHOCOCH_3 + Hg(OCOCH_3)_2 \xrightarrow[KCl]{} ClHg\overset{\displaystyle R}{C}HCH{=}O}$$

I

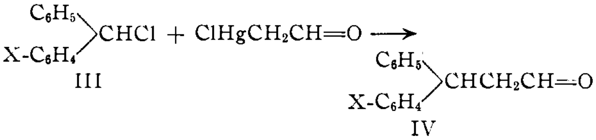


$$\mathrm{I + (C_6H_5)_3CCl \xrightarrow[\text{dry benzene}]{} (C_6H_5)_3C\overset{\displaystyle R}{C}HCH{=}O}$$

II

The method of synthesis was also successful with α-methyl- or ethyl-substituted chloromercurialdehydes to give (II, R = CH_3) or (II, R = C_2H_5).

Benzhydryl chloride (III, X = H) failed to undergo the reaction with (I, R = H) under the above conditions. However, when an equimolar amount of stannic chloride was added to the reaction mixture, reaction proceeded satisfactorily to give a 37% yield of (IV, X = H).



$$\mathrm{\begin{matrix}C_6H_5\\X\text{-}C_6H_4\end{matrix}\!>\!CHCl + ClHgCH_2CH{=}O \longrightarrow \begin{matrix}C_6H_5\\X\text{-}C_6H_4\end{matrix}\!>\!CHCH_2CH{=}O}$$

III IV

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[1] (a) Presented in part before the Organic Division of the American Chemical Society in Buffalo in March, 1952. Based on a Dissertation submitted by Marvin J. Hurwitz to Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. (b) Department of Chemistry, University of Illinois, Urbana, Illinois.

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

[3] S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

[4] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1946, p. 178 ff.

[5] H. W. Urry and N. Nicolaides, Abstracts of Papers, 118th Meeting, American Chemical Society, 1950, p. 17N.

[6] A. N. Nesmeyanov, I. F. Lutsenko and Z. M. Tumanova, *Izvest. Akad. Nauk S.S.R.R. Otdel Khim. Nauk*, 601 (1949) [*C. A.*, **44**, 7225*c* (1950)].