amined by glpc analysis. The significant data are summarized below. At 570° these four compounds were essentially the only constituents of the product mixtures. At 740° as much as 50% of the product mixtures consisted of unidentified materials. Pyrolysis of dienone 1 at 570° gave 70% conversion to a 3:2:1 mixture of 5:4:3. At the same temperature, 3 gave only 10% conversion, mainly to 4 and 5. Even at 740° less than half of 3 was rearranged (unidentified components taken into account), primarily to 4 and 5. About 30% of the *cis*-cyclopentanone (4) was converted to the *trans*-cyclopentanone (5) at 570°. At the same temperature, about 15% conversion of 5 to 4 was obtained. These were essentially the only products at this temperature. At 740°, both 4 and 5 led to a mixture containing a 6:1 ratio of 5:4 as about 75% of the mixture. There were traces of dienone 1 and cyclohexanone 3 in these products.

Base-Catalyzed Interconversion of Cyclopentanones 4 and 5.— About 10 mg of sodium metal was dissolved in 5 ml of dry methanol and 20 mg of the *trans*-cyclopentanone was added. The solution was heated to reflux for 17 hr, diluted with water, and extracted with pentane. The product was shown by glpc to be 92% *trans*- and 8% *cis*-cyclopentanone. Similar treatment of an 85% pure sample of 4 led to a product mixture indicated to be 83% 5 and 17% 4.

Irradiation of 7-Methylocta-1,6-dien-3-one (1).— A solution of 11 mg of 1 in 1.0 ml of purified hexane in a quartz test tube was degassed by bubbling prepurified nitrogen through the solution for 1 min with a pipet and sealed with a rubber serum cap. This solution was irradiated in a Rayonet reactor with a bank of sixteen 2537-Å bulbs for 1 hr. Glpc analysis indicated no change in the sample. Further irradiation with 3000-Å lamps for 4 hr caused formation of a white solid on the wall of the tube, but glpc assay failed to reveal any volatile products.

Another 10-mg sample of 1 in 5 ml of purified benzene in a 10-ml Pyrex flask was degassed as above. Acetone (2 drops) was added and the solution was irradiated at 3000 Å for 17 hr. Glpc examination again disclosed no volatile products.

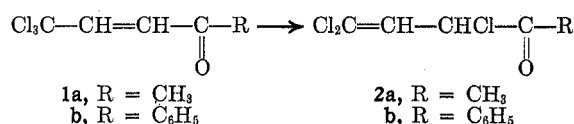# The Allylic Rearrangement of 3,3,3-Trichloro-1-propenyl Ketones

AKIRA TAKEDA AND SADAO TSUBOI

Department of Synthetics Chemistry, the School of Engineering, Okayama University, Okayama, Japan 700

The anionotropic allylic rearrangement of 3,3,3-trichloro-1-propenyl methyl ketone (1a) and 3,3,3-trichloro-1-propenyl phenyl ketone (1b) has been investigated. It afforded 1,3,3-trichloro-2-propenyl methyl ketone (2a) and 1,3,3-trichloro-2-propenyl phenyl ketone (2b), respectively. The isomerization was catalyzed by various solids, *e.g.*, silica gel, alumina, acid clay, cobaltous oxide, cupric oxide, ferric oxide, and iron and copper powder but not by metal oxides of more ionic character, *e.g.* calcium oxide, magnesium oxide. The rearranged products primarily reacted with nucleophiles as α-chloro ketones. Diethylamine and triethylamine, however, catalyzed the prototropic rearrangement of 2a and 2b to give 1,3,3-trichloro-1-propenyl methyl ketone (10a) and 1,3,3-trichloro-1-propenyl phenyl ketone (10b). The intermediate diethylamine salt of 2b (12) was isolated as a white powder and characterized. The transformation of 12 to 10b was complete within a few days when kept at room temperature.

Allylic rearrangements of 1,1,1-trichloro-2-propenes have been reported by several authors. The isomerization of 1,1,1-trichloro-2-methyl-2-propene to 1,1,3-trichloro-2-methyl-1-propene has been studied by Kundiger, *et al.*[1] The reaction might be catalyzed by such materials as silica gel, thionyl chloride, antimony pentachloride, and alkaline soft glass powder, or proceed pyrolitically. Hexachloropropene-1-^{14}C was isomerized by heating at 120° for several hours and by the chromatographical treatment on silica gel.[2] We have recently found that 1-acyl-3,3,3-trichloro-1-propenes (1) also undergo the allylic rearrangement by the action of solid supports of glpc to form 1-acyl-1,3,3-trichloro-2-propenes (2). The α hydrogen in 2 is highly activated by the influence of adjacent groups so that they are subject to further chemical change.

$$Cl_3C-CH{=}CH-\underset{\underset{O}{\|}}{C}-R \longrightarrow Cl_2C{=}CH-CHCl-\underset{\underset{O}{\|}}{C}-R$$

1a, R = CH₃   2a, R = CH₃
 b, R = C₆H₅   b, R = C₆H₅

This paper describes the catalytic transformation of 3,3,3-trichloro-1-propenyl methyl ketone (1a) and 3,3,3-trichloro-1-propenyl phenyl ketone (1b) to 1,3,3-trichloro-2-propenyl methyl ketone (2a) and 1,3,3-trichloro-2-propenyl phenyl ketone (2b) and discusses their structures and chemical properties.

The substrate 1a was heated on a bath at 120–180° in the presence of solid materials as catalyst and distilled under a reduced pressure (20–30 mm) in order to investigate their effect on the present transformation. Strongly ionic substances such as calcium oxide, magnesium oxide, and sodium chloride did not catalyze the reaction. On the other hand, the presence of less ionic materials such as cobaltous oxide, cupric oxide, and ferric oxide catalyzed the reaction considerably with the partial formation of resinous products. Silica gel was most eminent in the catalytic action among solid supports used. A small amount of 3,4-bis(2',2'-dichlorovinyl)-3-chloro-2,5-hexanedione (3) was usually produced as a by-product. A possible mechanism of the formation of 3 is tentatively given as shown in eq 1.
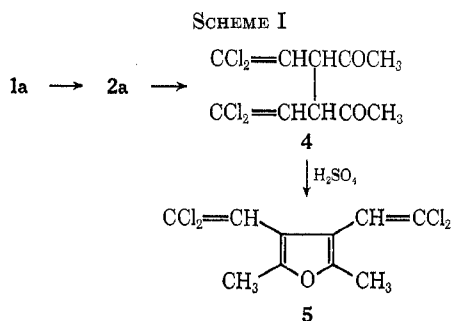

$$(1)$$
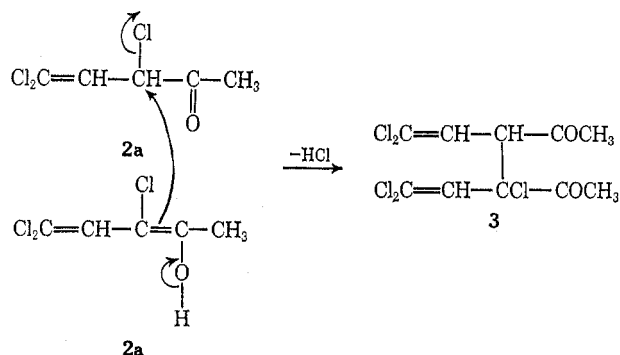
(1) (a) D. G. Kundiger and K. H. Groman, *J. Amer. Chem. Soc.*, **75**, 1744 (1953); (b) D. G. Kundiger and H. N. Haney, *ibid.*, **76**, 615 (1954).
(2) C. H. Shuford, Jr., D. L. West, and H. W. Davis, *ibid.*, **76**, 5803 (1954).

The isomerization has occurred also in the presence of iron and copper powder. The transformation of **1b** with the presence of silica gel was conducted at higher temperatures (170–220°) successfully.

The structures of **2a** and **2b** were elucidated by ir and nmr data and elemental analyses. The ir absorption of **2a** at 1730 cm^{-1} is consistent for isolated C=O indicating that the conjugation of C=C and C=O has disappeared as a result of the rearrangement. In the ir spectrum of **1a** absorptions due to ν (C=O, cisoid) and ν (C=O, transoid) are observed at 1700 and 1676 cm^{-1}, respectively.[3]

The nmr spectrum of **2a** is decidedly different from that of **1a**. While **1a**, measured in deuteriochloroform, exhibits a singlet at τ 7.60 (3, methyl protons) and an AB quartet with centers at τ 2.94 and 3.43 (2, vinyl protons, J = 14 Hz), **2a** exhibits a singlet at τ 7.68 (3, methyl protons), a doublet at τ 3.96 (1, vinyl proton, J = 9 Hz), and a doublet at τ 5.08 (1, methine proton, J = 9 Hz). When **1a** was treated with copper powder at 120–180° white crystals melting at 71–73° were obtained in 23% yield along with the isomerized product (**2a**, 10%). Spectral data and elemental analyses indicate that this compound is 2,5-dimethyl-3,4-bis(2′,2′-dichlorovinyl)furan (**5**) as is evidenced by the fact that **2a** also gives **5** on the treatment with copper powder in the absence of solvent. It is therefore postulated that the cyclization to **5** proceeds via 3,4-bis(2′,2′-dichlorovinyl)-2,5-hexanedione (**4**) (Scheme I). Actually, when
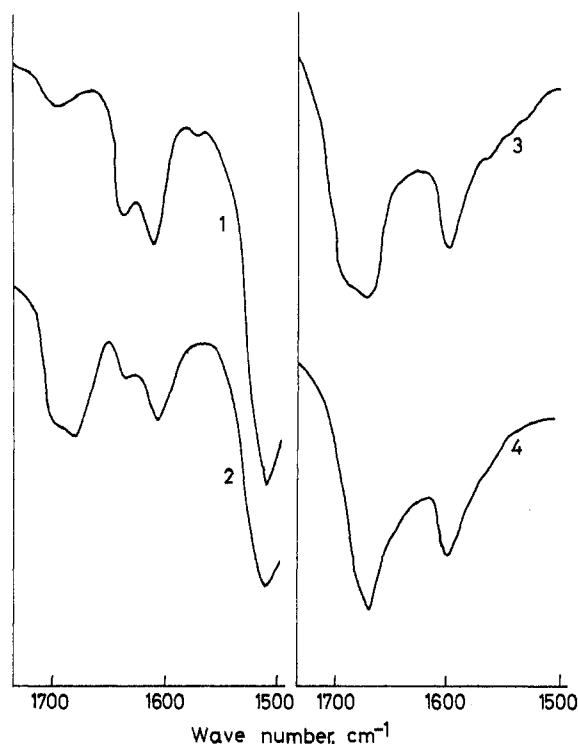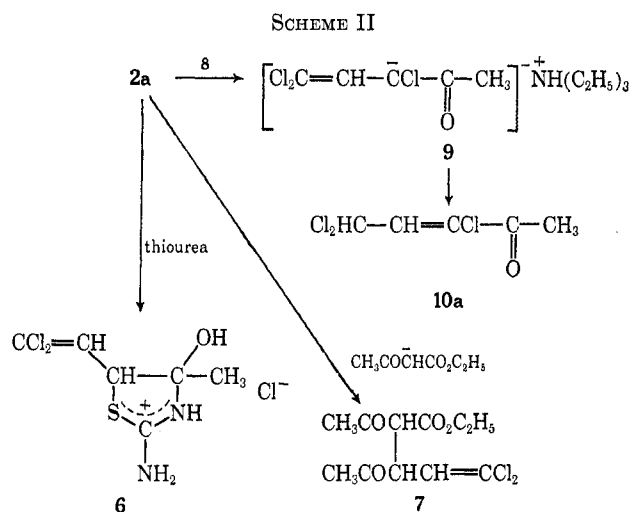
Figure 1.—The shifts in absorption bands of the amine salt (**12**) with time: (1) a few minutes after the formation, (2) 2 hr; (3) 2 days, (4) 2 weeks.

SCHEME I

$$\mathbf{1a} \longrightarrow \mathbf{2a} \longrightarrow \begin{array}{c} CCl_2=CHCHCOCH_3 \\ | \\ CCl_2=CHCHCOCH_3 \end{array}$$

4

$$\downarrow H_2SO_4$$

$$\underset{CH_3}{\overset{CCl_2=CH}{\diagdown}}\underset{O}{\diagup}\underset{CH_3}{\overset{CH=CCl_2}{\diagup}}$$

5

2a or **1a** was treated with copper powder in xylene, the intermediate (**4**) was produced in 35% yield. The cyclization of **4** to the furan (**5**) was realized also by the treatment with concentrated sulfuric acid. Uv absorption bands of **5** reveals the existence of the conjugated carbon–carbon double bond and furan ring [λ_{max} 219 mμ (ϵ 19,500) and 267 (18,000)]. The nmr spectrum of **5** is very simple, τ 3.56 (2, singlet) and τ 7.82 (6, singlet) in deuteriochloroform indicating its symmetrical structure as regards the ring. Furthermore, its furan ring resisted the hydrolysis with diluted sulfuric acid.[4] The increased stability of this compound might be attributable to the conjugation of two 2′,2′-dichlorovinyl groups with the furan ring. The present reaction may thus be an useful method for obtaining symmetrically substituted furan derivatives.

To investigate the reactivity of the rearranged product (**2a**) as an α-chloro ketone, it was allowed to react with several nucleophiles (Scheme II). It afforded

(3) R. D. Campbell and N. H. Cromwell, *J. Amer. Chem. Soc.*, **79**, 3456 (1957).

(4) The ring opening of furan derivatives is usually achieved by refluxing with 10% sulfuric acid (D. M. Young and C. H. F. Allen, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 220).

SCHEME II

$$\mathbf{2a} \xrightarrow{8} \left[Cl_2C=CH-\bar{C}Cl-\underset{O}{\overset{}{\underset{||}{C}}}-CH_3 \right]^{-}\overset{+}{N}H(C_2H_5)_3$$

9

$$\downarrow$$

$$Cl_2HC-CH=CCl-\underset{O}{\overset{}{\underset{||}{C}}}-CH_3$$

10a

(thiourea; (diagonal arrow)

$$\underset{NH_2}{\overset{CCl_2=CH}{\underset{\underset{S\overset{+}{\diagdown}\diagup NH}{CH-\underset{|}{\overset{OH}{C}}-CH_3}}{}}} Cl^{-}$$

6

$$CH_3CO\bar{C}HCO_2C_2H_5$$

$$CH_3CO\underset{|}{\overset{}{C}}HCO_2C_2H_5$$

$$CH_3CO\underset{|}{\overset{}{C}}HCH=CCl_2$$

7

2-amino-4-methyl-4-hydroxy-5-(2′,2′-dichlorovinyl)thiazoline hydrochloride (**6**) with thiourea and 3-carbethoxy-4-(2′,2′-dichlorovinyl)-2,5-hexanedione (**7**) with ethyl sodioacetoacetate, whereas the reaction of **2a** with triethylamine (**8**) in ether solution resulted in the formation of 1,3,3-trichloro-1-propenyl methyl ketone (**10a**) in 62% yield.
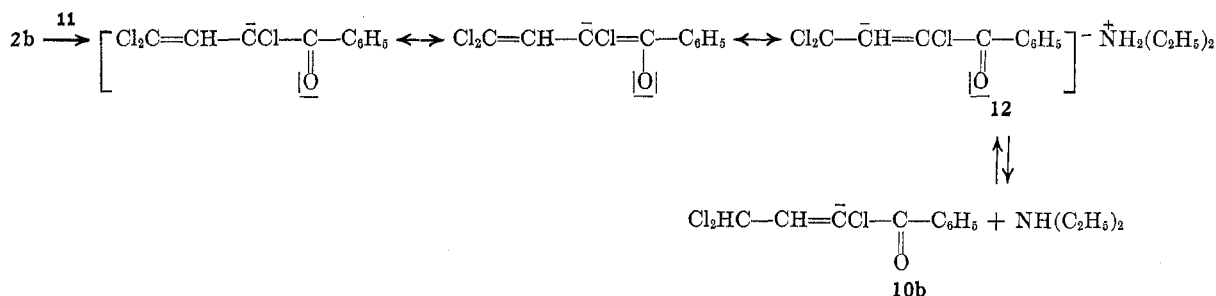
It should be noted that in the ir spectra of **10a** the absorption due to ν (C=O) is observed only at 1700 cm^{-1} which is indicative of the cisoid structure. It is presumed that the repulsive force between chlorine and carbonyl oxygen of **10a** caused the disappearance of the transoid structure.

The mechanism of the transformation of **2** to **10** may be postulated as follows. The α-methine proton in **2** is acidic enough to transfer to and protonate **8**. The tertiary ammonium salt (**9**) produced intermediately is then transformed to **10** gradually. The above postula-

SCHEME III

$$2b \xrightarrow{11} \left[Cl_2C=CH-\overset{|}{\underset{|O}{C}}Cl-\overset{|}{\underset{}{C}}-C_6H_5 \longleftrightarrow Cl_2C=CH-\overset{}{C}Cl=C-C_6H_5 \longleftrightarrow Cl_2C-\overset{|}{C}H=CCl-\overset{}{\underset{|O}{C}}-C_6H_5 \right]^- \overset{+}{N}H_2(C_2H_5)_2$$

$$\underset{12}{}$$

$$\updownarrow$$

$$Cl_2HC-CH=\overset{}{\bar{C}}Cl-\overset{}{\underset{O}{C}}-C_6H_5 + NH(C_2H_5)_2$$

$$\underset{10b}{}$$

tion has been evidenced by the fact that, in the reaction of 1,3,3-trichloro-2-propenyl phenyl ketone (2b) with diethylamine (11), the amine salt (12) was isolated as white crystals in 62% yield. Infrared absorption band of 12 originally observed at 1700 cm^{-1} (C=O, Nujol) has shifted to 1670 cm^{-1} in 1 day indicating that 12 has undergone the transformation to 10b partly while being kept at room temperature (see Figure 1). The distillation of 12 also gave 10b in 38% yield. The γ proton of 10b is mobile since the diethyl amine salt (12) was reproduced on addition of 11 to 10b (Scheme III).

Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were carried out by Mr. Eiichiro Amano of our laboratory. Analytical determinations by glpc were performed on Hitachi K-53 model gas chromatograph (3-mm o.d. × 1 m, 10% Apiezon Grease L on Chromosorb W), and preparative isolations by glpc were performed on Yanagimoto GCG-550T model gas chromatograph (3 mm o.d. × 2.25 m, 10% Apiezon Grease L on Chromosorb W). We are indebted to Dr. Akira Suzuki and Mr. Sigezo Simokawa, both of Hokkaido University, Sapporo, Japan, for nmr measurements. Microanalyses and spectral measurements of liquids were performed on samples collected by glpc.

Commercial grade materials were purchased and used as catalysts in the transformation without purification. 3,3,3-Trichloro-1-propenyl methyl ketone (1a) was prepared in 80% yield by the method of Salkind[5a] by treating chloroacetone[5b] with concentrated sulfuric acid: bp 95–100° (20 mm); mp 25–26° [lit.[5a] bp 93–94° (20 mm), mp 25–26°]; ir (liquid) 1700 (cisoid C=O), 1676 (transoid C=O), 1630 (C=C) and 737 cm^{-1} (C—Cl); nmr (CDCl$_3$) τ 2.94, 3.43 (q, 2, J = 14 Hz, –CH=CH–C=O), and 7.60 (s, 3). 3,3,3-Trichloro-1-propenyl phenyl ketone (1b) was prepared similar to the manners described in the literature:[5c] yield 81%; mp 98–99° (lit.[5c] mp 100°); ir (Nujol) 1652 (C=O), 1625 (C=C), 1595 (benzene C=C) and 740 cm^{-1} (C—Cl).

General Procedure for the Catalytic Transformation of 1a.— A mixture of equal amounts of 1a and the catalyst was heated on a bath at 120–180° and distilled under diminished pressure (20–30 mm). The distribution of 1a and 2a in the distillate was determined by the measurement of infrared absorbances at 1730 cm^{-1} (C=O) for 2a and at 737 cm^{-1} (C—Cl) for 1a, respectively. The effects of solid materials on the transformation are as follows [substances, amounts of distillate (%), contents of 2a (%) in distillate[6a]]: CuO, 16, 99; Fe, 16, 89; Cu, 33, 87; CoO, 33, 89; FeO, 23, 73; silica gel, 72, 58; alumina, 50, 73; acid clay, 93, 45; Celite 535, 93, 26; MgO, 90, 13; CaO, 93, 0; Na$_2$CO$_3$, 80, 0; FeS,[6b] 0, 0; PbO, 93, 5; NaCl, 86, 0; SOCl$_2$,[6c] 52, 73; HCl,[6d] 76, 34.

1,3,3-Trichloro-2-propenyl Methyl Ketone (2a).— A mixture of 50 g of 1a and 50 g of silica gel on one treatment as above yielded 35.9 g of crude product of ca. 58% purity. Similar treatment

repeated two times more afforded a product of at least 95% purity, yield 19.6 g (39%), bp 90–91° (19 mm). After distilling off a small amount of by-product (3, 1 g, see the next section) at 76° (15 mm), an analytical sample of the product was collected at 79–80° (12 mm) by fractional distillation using spinning-band column with the theoretical plate number of 70: n^{27}D 1.4951.

Anal. Calcd for C$_5$H$_5$Cl$_3$O: C, 32.04; H, 2.69. Found: C, 31.88; H, 2.82.

3,4-Bis(2',2'-dichlorovinyl)-3-chloro-2,5-hexanedione (3).— Analytical sample of the low-boiling fraction obtained in the above experiment was preparatively isolated by gas chromatograph: ir (liquid) 1721 and 1698 (C=O) and 1595 cm^{-1} (C=C).

Anal. Calcd for C$_{10}$H$_9$Cl$_5$O$_2$: C, 35.49; H, 2.68. Found: C, 35.48; H, 2.81.

1,3,3-Trichloro-2-propenyl Phenyl Ketone (2b).— From a mixture of 89 g (0.357 mol) of 1b and 90 g of silica gel, 35.4 g (40%) of a liquid distilling at 145–146° (5 mm) was obtained by the same treatment as described in the foregoing experiment with 1a: n^{27}D 1.5752; ir (liquid) 1690 (C=O) and 1618 cm^{-1} (C=C).

Anal. Calcd for C$_{10}$H$_7$Cl$_3$O: C, 48.13; H, 2.83. Found: C, 48.41; H, 3.03.

3,4-Bis(2',2'-dichlorovinyl)-2,5-hexanedione (4). (a) From 3,3,3-Trichloro-1-propenyl Methyl Ketone (1a).— Copper powder (6.6 g, 0.104 g-atom) was suspended in a solution of 1a (10.0 g, 0.053 mol) in 30 ml of xylene. The mixture was heated under reflux on an oil bath for 1 hr. After filtration, removal of xylene, and recovery of 1a (0.3 g, 3%) at 95–98° (20 mm), 3.0 g (37%) of a fraction distilling at 132–137° (20 mm) was collected: ir (liquid) 1725 (C=O) and 1620 cm^{-1} (C=C).

Anal. Calcd for C$_{10}$H$_{10}$Cl$_4$O$_2$: C, 39.51; H, 3.32. Found: C, 39.70; H, 3.30.

(b) From 1,3,3-Trichloro-2-propenyl Methyl Ketone (2a).— A solution of 2a (2.1 g, 0.011 mol) in 6 ml of xylene suspended with copper powder (1.4 g, 0.022 g-atom) was refluxed for 1 hr. After filtration and removal of the solvent, a fraction distilling at 100–120° (5 mm) was collected, yield 0.8 g. Analysis by glpc indicated that this fraction consisted of roughly equal portions of 4 and 5.

2,5-Dimethyl-3,4-bis(2',2'-dichlorovinyl)furan (5).— In 10 ml of concentrated sulfuric acid, 1.2 g (0.004 mol) of 4 was dissolved. After being kept at room temperature for 5 min the solution was poured onto cracked ice. The organic layer was extracted with ether several times and the extracts were dried over Na$_2$SO$_4$. Removal of the solvent gave a deep yellow solid. Recrystallizations of the crude product from petroleum ether (bp 50–70°) yielded 0.5 g (44%) of white crystals: mp 71–73°; bp 120° (2 mm); ir (Nujol) 1603 (C=C) and 1584 cm^{-1} (furan C=C); uv max (98% C$_2$H$_5$OH) 219 (ε 19,500) and 267 (18,000); nmr (CDCl$_3$) τ 3.56 (s, 2), and 7.82 (s, 6).

Anal. Calcd for C$_{10}$H$_8$Cl$_4$O: C, 42.00; H, 2.82. Found: C, 41.95; H, 2.90.

Transformation of 1a to 5 by the Action of Copper.— A mixture of 19.7 g (0.105 mol) of 1a and 20 g (0.315 g-atom) of copper powder was heated *in vacuo* at 90–110° at reflux. Heating was continued for 3 hr. The mixture was fractionally distilled to give 2.0 g (10%) of 2a and a fraction which distilled at 120° (2 mm) and solidified immediately as white crystals, mp 71–73°. This proved to be 5 by ir spectroscopy, yield 3.5 g (23%). The ir spectrum of this product was superimposable with that of 5.

Hydrolysis of 5.— A mixture consisting of acetic acid (10 ml), water (1 ml), 10% sulfuric acid (0.5 ml), and 0.5 g (0.0017 mol) of 5 was heated under reflux for 50 hr. On cooling 0.4 g of white crystals separated, mp 71–73° (from C$_2$H$_5$OH). No other product was detected in an appreciable amount. It did not show depression of mixture melting point with 5.

(5) (a) I. Salkind, *J. Russ. Phys. Chem. Soc.*, **30**, 906 (1898); (b) H. Gault and G. Mennicken, *C. R. Acad. Sci., Paris*, **229**, 1239 (1949); (c) W. Koenigs, *Chem. Ber.*, **25**, 795 (1892).

(6) (a) The remainder was mainly 1a. (b) Polymerization has occurred. (c) Ten grams of 1a was refluxed for 20 hr with 30 ml of thionyl chloride under nitrogen gas. (d) With continuous stream of dry hydrogen chloride 1a was heated at 100–110° for 15 hr.

2-Amino-4-methyl-4-hydroxy-5-(2′,2′-dichlorovinyl)thiazoline Hydrochloride (6).—To a solution of 0.8 g (0.011 mol) of thiourea in 22 ml of ethanol was added 1.8 g (0.010 mol) of 2a dropwise at 30–40°. The mixture was allowed to stand overnight. Removal of the solvent left a red-brown powder which on recrystallization from 80% ethanol gave 1.33 g (50%) of brown crystals. It showed one spot on tlc and became colorless after several recrystallizations from 80% C_2H_5OH: mp 192° dec: ir (Nujol) 3400 (OH), 2730 and 2600 (NH$^+$), 1650 (C=C), and 1610 cm^{-1} (NH$_2$).

Anal. Calcd for $C_6H_9Cl_3N_2OS$: C, 27.34; H, 3.44. Found: C, 27.49; H, 3.59.

3-Carbethoxy-4-(2′,2′-dichlorovinyl)-2,5-hexanedione (7).—Sodium (0.9 g, 0.039 g-atom) was dissolved in 13 ml of absolute ethanol. Ethyl acetoacetate (4.9 g, 0.038 mol) was added to this solution. At reflux temperature, 7 g (0.037 mol) of 2a was dropped into the mixture and refluxing was continued for 1 hr. The sodium chloride precipitate was removed by filtration. After evaporation of the solvent and recovery of 2a (1.5 g, 21%), an oil distilling at 133–135° (2.5 mm) was obtained: yield 1.2 g (11%); n^{25}D 1.4860; ir (liquid) 1730 (ester C=O), 1710 and 1684 (C=O), 1648 cm^{-1} (C=C).

Anal. Calcd for $C_{11}H_{14}Cl_2O_4$: C, 46.99; H, 5.02. Found: C, 46.87; H, 4.77.

1,3,3-Trichloro-1-propenyl Methyl Ketone (10a).—A solution of 2.2 g (0.022 mol) of triethylamine in 3 ml of anhydrous ether was added dropwise to a solution of 4 g (0.021 mol) of 2a in 5 ml of anhydrous ether cooled in an ice bath. After standing overnight it was filtrated to remove a trace of a brown precipitate. It was washed several times with water and dried with Na_2SO_4. Distillation gave a fraction of oil boiling at 90–91° (15 mm): yield 2.5 g (63%); n^{29}D 1.5049; ir (liquid) 1700 (C=O), and 1615 cm^{-1} (C=C); uv max (cyclohexane) 239 mμ (ϵ 9720), 322 (39); nmr (CDCl$_3$) τ 2.94 (d, 1), 3.44 (d, 1), and 7.51 (s, 3).

Anal. Calcd for $C_5H_5Cl_3O$: C, 32.04; H, 2.69. Found: C, 32.02; H, 2.90.

1,3,3-Trichloro-1-propenyl Phenyl Ketone (10b).—A solution of 3 g (0.012 mol) of 2b in 5 ml of ether was added with ice cooling to 3.7 g (0.037 mol) of 8 dissolved in 10 ml of anhydrous ether. The reaction mixture was kept cold for 30 min and then washed thoroughly with water. Removal of the solvent left a yellow liquid which on distillation gave 1.5 g (50%) of a yellow oil, bp 128–131° (2 mm). Microanalyses and spectral measurements were performed on samples collected by column chromatography (silica gel, hexane): n^{24}D 1.5768; ir (liquid) 1670 (C=O), 1618 (C=C), and 1595 cm^{-1} (benzene C=C).

Anal. Calcd for $C_{10}H_7Cl_3O$: C, 48.13; H, 2.83. Found: C, 47.91; H, 2.75.

Addition Product of Diethylamine with 2b (12).—To a solution of diethylamine (1.1 g, 0.015 mol) in 2 ml of anhydrous ether, 2b (1.0 g, 0.004 mol) dissolved in 2 ml of ether was added dropwise with ice cooling. A brown precipitate was separated immediately. It was gathered by filtration and washed thoroughly with anhydrous ether on filter paper and air-dried, giving 0.8 g (62%) of the crude product: mp 50° dec; ir (Nujol) 2480 and 2350 (NH$^+$), 1700 (C=O, very weak), 1640 (C=C), and 1610 cm^{-1} (benzene C=C). Because of rapid decomposition this product could not be purified for analysis, and so its physical constants may be in doubt.

Shift of ir absorption bands in C=O region with time is graphed on Figure 1 in the text.

It is insoluble in water, acetone, tetrahydrofuran, and ether, but soluble in benzene and chloroform, and very soluble in ethanol.

A Novel Reaction between Benzil and Certain Nucleophilic Agents in N,N-Dimethylformamide[1]

John C. Trisler, Jiin Duey Cheng, and Ben F. Freasier

*Lousiana Polytechnic Institute, Ruston, Louisiana 71270*

Benzil reacts with certain nucleophiles (phenoxide, *t*-butoxide, and hydroxide) in N,N-dimethylformamide to yield, in each case, benzoin benzoate (3) and the corresponding benzoylated nucleophile. *p*-Methoxybenzil reacts with sodium phenoxide to form *p*-methoxybenzoin anisate (5) and phenyl benzoate.

Perhaps the best known reaction of benzil with a nucleophile is that with hydroxide ion in which rearrangement occurs giving the conjugate base of benzilic acid.[2] Alkoxides are less successful in effecting the corresponding benzilic ester rearrangement except for those which have little or no tendency to transfer hydride ion. Thus, *t*-butoxide ion and methoxide ion react with benzil in alcoholic or benzene solution to yield the corresponding benzilic ester, whereas alkoxides containing more labile α hydrogens (*e.g.*, ethoxide and isopropoxide) lead to reduction products.[3] It is reported that the reaction between benzil and *t*-butoxide ion in diethyl ether results in the formation of benzilic acid.[4] Phenoxide ion fails to react with benzil in alcoholic or benzene solution, presumably owing to insufficient basicity on the part of the nucleophile.[4,5]

Phenoxide ion and benzil are likewise unreactive in

dimethyl sulfoxide (DMSO) at room temperature. A reaction occurs at higher temperatures, although the products obtained do not incorporate phenoxide.[6,7] Phenoxide ion functions as a base to generate dimsyl ion, which then reacts with benzil to form 3-benzoyl-2, 4,5-triphenylfuran (1), *cis*-α,β-dibenzoylstyrene (2), benzoic acid, and benzilic acid.
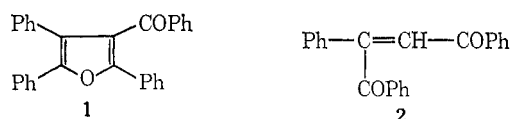
The present investigation was initiated to further confirm the necessity of DMSO to the formation of the products in the above reaction. In this respect the behavior of phenoxide ion toward benzil has been observed in a number of solvents. In the ethereal solvents, dimethoxyethane and diglyme, no reaction is en-

(1) Taken in part from the M.S. Thesis of J. D. Cheng.

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