zations from benzene–petroleum ether (b.p. 60–80°). This material showed no depression of melting point when mixed with the products from A and B above. The contents of the column were eluted with benzene and the filtrate contained 0.20 g. of yellow solid, m.p. 195–200°, from which a few crystals of pure tri-1-naphthylsilane (identified by a mixed melting point) were obtained after recrystallization from ethanol.

Tri-1-naphthylchlorosilane and 1-Naphthyllithium.—Ten grams (0.022 mole) of tri-1-naphthylchlorosilane was added to the suspension resulting from mixing 0.1 mole of 1-bromonaphthalene to 0.1 mole of n-butyllithium in ether, and refluxed for three days. Color Test I[19] was then negative. The mixture was poured into crushed ice and dilute hydrochloric acid and the layers were separated. The ether layer was steam distilled and the residue extracted with ether. After removal of the solvent from the ether extract and crystallization from petroleum ether (b.p. 90–115°), 7.5 g. (75%), in three crops, of crude tri-1-naphthylchlorosilane, m.p. 201–203°, was recovered, which showed no depression of melting point when mixed with an authentic specimen.

1-n-Butylnaphthalene[16] was isolated from these runs. Apparently the failure of this experiment is due to the faster rate of the coupling reaction of 1-naphthyllithium with n-butyl bromide as compared to the desired reaction of 1-naphthyllithium with tri-1-naphthylchlorosilane.

When 1-naphthyllithium made by the direct procedure[9] was mixed with tri-1-naphthylchlorosilane and baked at 150–180° for three days, no isolable products have yet been obtained from the black tars. However, tetra-o-tolylsilane was obtained under similar conditions and it is possible that tetra-1-naphthylsilane may yet be made by modifying the conditions.

Tri-1-naphthylsilanol and Formic Acid.—Ten grams (0.023 mole) of tri-1-naphthylsilanol and 100 ml. of 99–100% formic acid were mixed and refluxed for 15 hours. The solution was diluted with water, neutralized with sodium carbonate, and extracted with benzene. The benzene layer was concentrated and allowed to stand. After two days, 8.5 g. (85%) of tri-1-naphthylsilanol (determined by a mixed melting point) was recovered in two crops.

Tri-1-naphthylsilane and Potassium Hydroxide in Piperidine.[3]—The reagent was made by dissolving one pellet of potassium hydroxide in 3 ml. of piperidine containing 5 drops of water. When about 0.05 g. of tri-1-naphthylsilane was added and the mixture warmed to effect solution, no gas evolution was noted even after standing for several days. Under corresponding conditions, tri-o-tolylsilane showed no gas evolution, while triphenylsilane gave an immediate, rapid stream of gas.

In connection with some rate studies by G. E. Dunn, this evolution of hydrogen has been observed in a series of nonsterically-hindered silanes.

Hydrolysis of Tri-1-naphthylchlorosilane and Triphenylchlorosilane.—Stock solutions of 7.00 g. (0.0158 mole) of tri-1-naphthylchlorosilane in 1 l. of Merck reagent grade acetone and 12.00 g. (0.0406 mole) of triphenylchlorosilane in 1 l. of the same solvent were prepared and placed in a 25° thermostat. Five ml. of water per 100 ml. of stock solution was added and 25-ml. aliquots were removed at timed intervals and titrated with 0.0536 N sodium hydroxide using phenolphthalein as the indicator. Even after five days the tri-1-naphthylchlorosilane run did not show any increase in the consumption of base over the value obtained at zero time. The reading at zero time was 0.25 ml. and the blank, using the same concentration of acetone and water, was 0.20 ml. The triphenylchlorosilane aliquot at zero time required a volume of base equivalent to 100% hydrolysis. This hydrolysis of the triphenylchlorosilane may not have proceeded at an appreciable rate in the aqueous acetone, but, if not, reaction must have occurred during the titration with the weak base. Since tri-1-naphthylchlorosilane was unaffected by the low concentration of base, these experiments indicate the relative stability of these two silicon compounds toward dilute alkali.

The solvent from the acetone solutions of tri-1-naphthylchlorosilane was allowed to evaporate at room temperature. Well-formed crystals were isolated directly and these melted at 206–207°, and showed no depression of melting point when mixed with an authentic specimen.

(19) H. Gilman and F. Schulze, This Journal, 47, 2202 (1925).

A Study of the Friedel–Crafts Synthesis with Alkoxychloroalkanes[1]
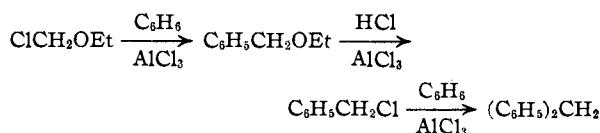
By Clarence T. Mason and Lewis A. Gist, Jr.

The behavior of alkoxychloroalkanes in a Friedel–Crafts reaction with benzene under varying conditions is used to explain the apparent discrepancies found in the earlier literature. The reaction does not take place through disproportionation of the alkoxychloromethane since: (1) dichloromethane could not be isolated, and (2) dibutoxymethane does not react in the Friedel–Crafts reaction under conditions comparable to those used for the alkoxychloromethane. Under similar conditions, alkoxychloromethanes and alkoxy-1-chloroethanes give analogous reactions, indicating that the mechanism of the reaction does not involve the elimination of hydrogen chloride to give an intermediate vinyl ether. The chlorine in alkoxy-1-chloroalkanes can react with benzene at low temperatures to give benzyl alkyl ethers, while under the same conditions the chlorine in 1-alkoxy-2-chloroethane does not react. Under more drastic conditions the latter suffers rupture of the carbon–oxygen bond.

Introduction

The stability of alkoxychloromethanes in the presence of easily hydrolysable metal halides has already been established,[2a,b,3,4] but at different temperatures, reaction times, and catalyst concentrations, many products are possible resulting from chloromethylation, condensation, polymerization, and decomposition of the alkoxychloromethane.

Verley[2a] reported isolating diphenylmethane as the chief product of the reaction of ethoxychloro-

methane with an excess of benzene in the presence of aluminum chloride and showed the presence of benzyl chloride and small amounts of benzyl ethyl ether. The latter he postulated as being split to give benzyl chloride, which condensed with the benzene to give diphenylmethane.

$$ClCH_2OEt \xrightarrow[AlCl_3]{C_6H_6} C_6H_5CH_2OEt \xrightarrow[AlCl_3]{HCl}$$

$$C_6H_5CH_2Cl \xrightarrow[AlCl_3]{C_6H_6} (C_6H_5)_2CH_2$$

Huston and Friedemann,[5] using the same reactants, found anthracene and diphenylmethane as the chief products, but did not isolate benzyl

(1) A portion of this paper was presented before the Organic Section of the American Chemical Society, September, 1950.

(2) (a) M. A. Verley, Bull. soc. chim., [3] 17, 914 (1897); (b) M. Sommelet, Compt. rend., 157, 1443 (1913).

(3) E. I. du Pont de Nemours and Co., British Patent 423,520, Feb. 4, 1935; C. A., 29, 4374⁹ (1935).

(4) F. Straus and T. Thiel, Ann., 525, 151 (1936).

(5) R. C. Huston and T. E. Friedemann, This Journal, 38, 2527 (1916).

ethyl ether. They suggested that ethoxychloromethane was decomposed into formaldehyde which, with benzene, gave diphenylmethane and anthracene.

$$ClCH_2OEt \xrightarrow{AlCl_3} HCHO \xrightarrow[C_6H_6]{AlCl_3} (C_6H_5)_2CH_2 + C_{14}H_{10}$$
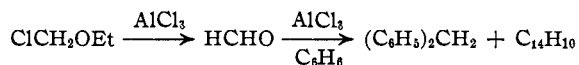
Sommelet[2b] treated methoxy-, ethoxy- and propoxychloromethane with benzene, using aluminum chloride in carbon disulfide, and obtained the corresponding benzyl alkyl ethers in yields as high as 30%.

A systematic investigation of the behavior of alkoxychloroalkanes in the Friedel–Crafts synthesis should explain some of these apparent discrepancies in the literature,[2a,b,5] and furnish some information which might help to explain the mechanism of their reaction. The behavior of these halogenated ethers in the presence of aluminum chloride is particularly interesting in view of their polyfunctional character which theoretically permits the formation of a coördinated complex with the catalyst in two positions: at the chlorine and the oxygen atoms. Any of the above mentioned reactions can be expected, depending upon the position of catalytic activity.

In the present investigation ethoxy-, propoxy- and butoxychloromethane; 1-ethoxy- and 1-butoxy-1-chloroethane; and 1-ethoxy-2-chloroethane reacted with benzene in the presence of aluminum chloride.

Discussion

The yields of the products isolated from the Friedel–Crafts reactions of alkoxychloromethanes were: benzyl chloride, 3–17%; dibutoxymethane, traces to 54%; benzyl ethyl ether, traces to 4%; benzyl propyl ether, 7–13%; benzyl butyl ether, 3–36%. The only significant difference in the reactions involving the various alkoxychloromethanes was the isolation of dibutoxymethane when butoxychloromethane was used.

The presence of large quantities of aluminum-free polymerization products may be explained by the Friedel–Crafts reaction of benzyl chloride with either itself or benzyl alkyl ether, yielding $C_6H_5CH_2-(C_6H_4CH_2)_n-C_6H_4CH_2Cl$ or branched analogs. Saturating the reaction mixture with hydrogen chloride before adding aluminum chloride did not affect the yield of polymer appreciably, but it did decrease the yield of ether. Two observations pointed to the essential non-cleavage of the hemiacetal chloride by hydrogen chloride: (1) the fact that a 55% yield of dibutoxymethane was isolated, its precursor being butoxychloromethane; (2) non-formation of dichloromethane in a comparable experiment wherein benzene was not added.

The absence of dichloromethane in the reaction product in the absence of benzene, and the fact that dibutoxymethane was found experimentally not to react with benzene in a Friedel–Crafts reaction under these conditions to give butyl benzyl ether, ruled out any possibility of disproportionality of the hemiacetal chloride (into dichloromethane and dialkoxymethane) or any large reaction of the dialkoxymethane with benzene and aluminum chloride.

Dibutoxymethane was isolated in largest yields from reactions conducted at sub-zero temperatures and short reaction time, and thus could be assumed not to be a result of any intermolecular rearrangement of butoxychloromethane. It was shown, instead, to be a result of the water hydrolysis of the butoxychloromethane when the Friedel–Crafts reaction mixture was treated with ice and hydrochloric acid. To prove this, freshly-distilled butoxychloromethane was hydrolyzed with ice and hydrochloric acid and the product isolated in the usual way. As found by Pudovik, et al.,[6] dibutoxymethane was isolated in 65–75% yield. Verley[2a] and Huston and Friedemann,[5] using ethoxychloromethane, did not isolate the relatively more unstable and more water-soluble diethoxymethane.

Thus the amount of dibutoxymethane found was an index of the degree of condensation of the butoxychloromethane in that when the latter did not condense, it reacted with the acid–ice mixture in the hydrolysis step to form dibutoxymethane. The following table is a brief summary of the reaction products formed when butoxychloromethane and benzene were condensed under varying conditions of reaction time, temperature and catalytic concentration.
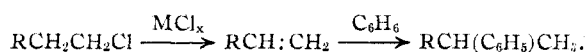
TABLE I
SUMMARY OF REACTION PRODUCTS

Mole concn. each per mole of ether AlCl₃	C₆H₆	CS₂	Reaction temperature in °C.	Reaction time in hours	Dibutoxymethane, %	Butyl benzyl ether, %	Others
1.00	1.00	2.5	−5 to 10	8	None	Traces	
0.25	2.00	3.4	−5 to room	20	None	....	
0.25	2.00	6.8	−5 to room	18	None	....	
1.00	1.00	5.2	−5	3	54	15	
0.45	1.10	11.9	−5	8	13	30	Benzyl chloride 19%
0.25	1.10	1.9	−5 to 5	5	40	9	Benzyl chloride 8%
1.00	2.00	3.4	−40 to −30	17	Traces	37	

These findings are in agreement with those of previous investigators,[2a,b,5] and what appear to be discrepancies arise through limits of the investigations. At the temperatures used by Verley[2a] small quantities of the ether may be obtained, while temperatures much above 0°, as reported by Huston and Friedemann[5] (they used 43°) greatly decrease the stability of the halogenated ethers and thus favor side reactions. It has been found, however, that the method of Sommelet[2b] although poor, is by far the most effective for the production of the benzyl alkyl ether. When carbon disulfide is used as a solvent and sub-zero temperatures maintained over long periods of time, fair yields of the ether may be obtained.

Considering the fact that the activity of the halogen in alkoxychloromethane is of the order of reactivity of that in an acid chloride, it is surprising that a clear cut reaction to give benzyl alkyl ether does not occur. A probable mechanism has been suggested for alkylation in the Friedel–Crafts reaction involving the splitting of hydrogen chloride from the alkyl halide to give an olefin which subsequently reacted with the aromatic ring[7]

(6) A. N. Pudovik, V. I. Nikitana and S. Kh. Aigistova, Zhur. Obschchei Khim. (J. Gen. Chem.). 19, 279 (1949); C. A., 43, 6568b (1949).

(7) Roger Adams, et al., "Organic Reactions," Vol. III. John Wiley and Sons. Inc., New York, N. Y., 1946, pp. 6–7.

$$\text{RCH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{MCl}_x} \text{RCH:CH}_2 \xrightarrow{\text{C}_6\text{H}_6} \text{RCH(C}_6\text{H}_5)\text{CH}_3.$$

Such an intermediate as postulated above is not possible in a condensation involving alkoxychloromethanes, and could explain why alkylation yields are low and polymerization high, even at reaction temperatures of $-40°$. Halogenated ethers related to acetaldehyde or higher aldehydes would permit a test of this prediction, since they would permit formation of the double bond (CH_2:CHOR from CH_3CHClOR); but when these compounds (R = Et, Bu) were tested, it was found that yields of alkyl α-methylbenzyl ethers and polymers were of the same order as from the formaldehyde analogs. Thus there is no reason to believe that the reaction mechanism was different in the two cases, and the possibility that alkylation occurs *via* the unsaturated ether is eliminated.

The concentration of the catalyst has a great effect on the reaction. In the presence of benzene, aluminum chloride is not appreciably soluble at $0°$ in a mixture of alkoxychloromethane and carbon disulfide. In the absence of benzene, one mole of aluminum chloride added at $-40°$ to one mole of alkoxychloromethane in carbon disulfide and the mixture allowed to warm slowly to $0°$, gives a bright green solution. A small amount of benzene added to the above solution at $-40°$ gives a violent exothermic reaction yielding only polymeric materials. It is reasonable to assume that the smaller ratio of catalyst forms a coördinate complex on only one functional group of the alkoxychloromethane, and that in the presence of benzene there is a reaction. With higher ratios of catalyst and in the absence of benzene, coördinates are formed on both the ethereal oxygen and the chlorine atoms leading to decomposition when benzene is added.

In the 1-alkoxy-1-chloroalkanes so far discussed the two positions capable of forming coördinate complexes with the catalyst are both attached to the same carbon atom. This is not the case with 1-ethoxy-2-chloroethane and a comparison of its behavior with that of the 1-alkoxy-1-chloroalkane in a Friedel–Crafts reaction with benzene should prove interesting. 1-Ethoxy-2-chloroethane does not react under conditions similar to those in the reaction of 1-alkoxy-1-chloroalkane. Under the more drastic conditions of excess aluminum chloride and refluxing at the boiling point of benzene, 1,2-diphenylethane and ethylbenzene are obtained as reaction products, indicating that here both the carbon–oxygen and the carbon–chlorine bonds are cleaved. It follows then that the chlorine in the α-halogenated ether is active enough in the Friedel–Crafts reaction to couple without rupture of the carbon–oxygen bond, but that the chlorine in the 2-position is less active, and that conditions necessary for its condensation also cause rupture of the carbon–oxygen bond.

Experimental

The compounds used in this work are listed below with their boiling points, d^{22}_4 and n^{18}D, respectively: ethoxychloromethane, 84°, 1.019, 1.4040; propoxychloromethane, 109°, 0.9894, 1.4106; butoxychloromethane, 134°, 0.9661, 1.4141; 1-ethoxy-1-chloroethane, 43° (124 mm.), 0.9495, 1.4021; 1-butoxy-1-chloroethane, 34° (7 mm.), 0.9339, 1.4126; 1-ethoxy-2-chloroethane, 108°, 1.0310, 1.4100.

Reaction of a 1-Alkoxy-1-chloroalkane with Benzene and AlCl₃.—Into a 500-ml. three-neck round bottom flask fitted with a mechanical stirrer, thermometer and HCl trap was placed 260 g. (3.4 moles) CS₂, 35 g. (0.29 mole) freshly distilled butoxychloromethane, and 24 g. (0.31 mole) benzene. Stirring was started and the solution chilled to $-5°$. During the period of chilling, 17 g. (0.13 mole) (Baker C.P.) AlCl₃ was ground and weighed into eight approximately equal portions which were placed in stoppered vials and added to the cold reaction mixture at one hour intervals. The temperature was kept within two degrees of $-5°$. One hour after the addition of the last portion of AlCl₃ (8 hours) the reaction mixture was poured onto crushed ice and HCl. When the color had been discharged the two layers were separated, the carbon disulfide layer washed 3 times with water, and the solvent removed under partial vacuum at 20°. The residue was dissolved in isopropyl ether, washed with 5% NaOH, twice with water, dried over calcium chloride and vacuum fractionated; yield, C₆H₅CH₂-Cl, b.p. 51° (10 mm.), 7 g., 19%; dibutoxymethane, b.p. 63° (10 mm.), 3 g., 13%; benzyl butyl ether, b.p. 85° (10 mm.), 14 g., 30%. NOTE: Modification of the above reaction gave the products indicated in Table I.

Butoxychloromethane with Benzene, HCl and AlCl₃.—Into the usual apparatus fitted with an inlet tube for HCl, was placed 260 g. (3.4 moles) of CS₂, 56 g. (0.46 mole) of butoxychloromethane and 71.6 g. (0.92 mole) of benzene. The mixture was cooled to 0° and HCl passed in slowly. To the cold mixture was added 30.8 g. (0.23 mole) AlCl₃ in small portions such that the temperature did not rise above 2°. HCl was passed in for eight hours after which time the reaction mixture was treated as above; yield, dibutoxymethane, 20 g., 54.5%; benzyl butyl ether, 4 g., 5.3%; and a polymeric residue.

Butoxychloromethane with AlCl₃ and HCl.—CS₂, 130 g. (1.7 moles) and 30.5 g. (0.25 mole) of freshly distilled butoxychloromethane were cooled to 0° and HCl passed in slowly. To this was added 17 g. (0.13 mole) of AlCl₃ in small portions, keeping the temperature below 2°. After eight hours the reaction mixture was poured onto crushed ice and isolated as above; yield, dibutoxymethane, 10 g., 50%; trioxymethylene, butyl alcohol and a few drops of a heavy oil.

Dibutoxymethane with Benzene and AlCl₃.—CS₂ 130 g. (1.7 moles), 120 g. (0.75 mole) dibutoxymethane and 78 g. (1.0 mole) of benzene were stirred at $-5°$, and 26 g. (0.19 mole) of AlCl₃ in small quantities was added, keeping the temperature at 0°. After five hours the reaction mixture was decomposed as previously. No reaction occurred, and recovery of dibutoxymethane was almost 100%.

1-Ethoxy-2-chloroethane and C₆H₆ and AlCl₃.—(A) To 54.3 g. (0.5 mole) of 1-ethoxy-2-chloroethane and 94 g. (1.2 moles) of benzene at $-5°$ is slowly added 17 g. (0.13 mole) of AlCl₃. No reaction could be detected. The mixture was allowed to warm to room temperature and then heated under reflux for six hours, allowed to stand overnight, heated for two hours, and hydrolyzed as previously. No 1-ethoxy-2-phenylethane could be detected.

(B) To 54.3 g. (0.5 mole) of 1-ethoxy-2-chloroethane and 94 g. (1.2 moles) benzene at 0° is slowly added 73 g. (0.55 mole) of AlCl₃, the mixture allowed to warm to room temperature and then refluxed eight hours. After standing overnight the mixture was hydrolyzed as before, dried, and the products separated by distillation; yield, ethylbenzene, b.p. 135°, d^{22}_4 0.867, n^{18}D 1.4902, 20 g., 33.7%; 1,2-diphenylethane, b.p. 284–290°, m.p. 51–52°, 10 g., 11%; 1-ethoxy-2-chloroethane, b.p. 108–109°, 15 g.

AlCl₃ and Butoxychloromethane in the Absence of Benzene.—When 1 mole of AlCl₃ is added to a mixture of 1 mole of butoxychloromethane and 3.4 moles of CS₂ at $-40°$ and the mixture allowed to warm to 0° over a three-hour period, the catalyst dissolves to give a bright green solution. Chilling again to $-40°$ fails to cause precipitation of the catalyst. NOTE: Addition of cold benzene dropwise to the mixture at $-40°$ produces a violent exothermic reaction from which only polymeric substances can be isolated.

Identification of Dibutoxymethane.—Five grams of the compound suspected of being dibutoxymethane was decomposed by refluxing 0.5 hour with 10 cc. of 5% H₂SO₄. After steam distillation the alcohol was extracted from the distillate, and the 3,5-dinitrobenzoate prepared, purified by washing the ethereal solution with 5% NaHCO₃, and crystallized from methyl alcohol. The melting point and

mixed melting point with an authentic sample of alcohol were determined. Butyl 3,5-dinitrobenzoate, m.p. 60°, mixed melt 61°.

A second 5-gram sample of the unknown was added dropwise to 10 cc. of hot 50% H_2SO_4, the volatile materials distilled into ethyl alcohol and the 2,4-dinitrophenylhydrazone of formaldehyde was obtained. After recrystallizing from ethyl alcohol the melting and mixed melting points were taken: formaldehyde 2,4-dinitrophenylhydrazone, m.p. 164°, mixed melt, 164°.

Identification of Benzyl Alkyl Ether.—The product, a sample of which gave a negative test for halogen (alcoholic $AgNO_3$) when oxidized with basic $KMnO_4$, gave benzoic acid, which proved the presence of the benzyl radical.

The presence of oxygen was determined by the method of Davidson.[8] The benzyl ether was then cleaved at the oxy-

gen bond by refluxing 5 cc. with a mixture of 5 cc. of acetic anhydride, 5 cc. of acetic acid and 1 cc. of concentrated H_2SO_4 for four hours. The reaction mixture was then cooled and dissolved in 50 cc. of ether, washed with 10% $NaHCO_3$ until the washings were basic, twice with water, the ethereal solution fractionated and the two acetate esters collected. Boiling points, densities, and refractive indices were determined on the esters after which they were treated with 3,5-dinitrobenzoic acid to give the solid benzoates: Benzyl 3,5-dinitrobenzoate, m.p. 110°, mixed melt 111°; butyl m.p. 60°, mixed melt 61°; propyl m.p. 73°, mixed melt 74°; ethyl m.p. 93°, mixed melt 93°.

(8) David Davidson. *Ind. Eng. Chem., Anal. Ed.,* **12**, 40 (1940).

The Stereoisomeric Dibromides and α-Bromo Derivatives of Benzalacetophenone and the Mechanism of Dehydrohalogenation

BY ROBERT E. LUTZ, DAVID F. HINKLEY[1a] AND ROBERT H. JORDAN[1b]

A second and non-crystalline (*cis*) α-bromobenzalacetophenone has been obtained by sunlight inversion of the known (*trans*) crystalline form. It is formed in small amounts in the potassium acetate dehydrohalogenation of the high-melting benzalacetophenone dibromide but it is not obtained in the similar dehydrohalogenation of the low-melting dibromide. The ultraviolet absorption characteristics and interconversions of the isomers are discussed in relation to configuration. The assignment of configurations to the benzalacetophenone dibromides is made on the basis of differing behaviors on dehydrohalogenation where two competing mechanisms are suggested.

This investigation stemmed from a study of the possibility of stereochemical guidance in the reactions involved in the preparation of the diastereoisomeric α,β-dimorpholinylbenzylacetophenones,[2] and from the recent study of *cis*-benzalacetophenone.[3]

The higher-melting benzalacetophenone dibromide (m.p. 159–160°) (II) is the chief product in bromination of *trans*-benzalacetophenone.[4] The lower-melting isomer (m.p. 123–124°) (I) is formed at the same time in very small amounts but is difficult to isolate in pure condition from the mixture; it can be obtained in quantity from the much more favorable mixture of stereoisomers produced by the addition of hydrogen bromide under controlled conditions to the crystalline α-bromobenzalacetophenone (III)[4b,c] which is now shown to be *trans*.

The elimination of hydrogen bromide from the high-melting dibromide (II) by means of potassium acetate[4c] gives a mixture from which has been isolated the crystalline α-bromobenzalacetophenone, m.p. 41–42°, here to be designated as the *trans*-isomer (III). In a repetition of the experiment under controlled conditions this mixture was ob-

(1) (a) du Pont Company Fellow in Chemistry, 1950–1951; (b) at University of Virginia Medical School.

(2) *Cf.* (a) N. H. Cromwell, *Chem. Revs.,* **38**, 83 (1946); (b) R. E. Lutz and W. R. Smithey. *J. Org. Chem.,* **16**, 51 (1951); (c) R. H. Jordan. R. E. Lutz and D. F. Hinkley. *ibid.,* in press.

(3) (a) R. E. Lutz and R. H. Jordan, THIS JOURNAL, **72**, 4090 (1950). *Cf.* also the *cis*- and *trans*-benzalacetophenone semicarbazones [I. M. Heilbron and F. J. Wilson. *J. Chem. Soc.,* **101**, 1482 (1912); **103**, 1504 (1913)] and the β-methoxybenzalacetophenone derivatives [C. Dufraisse and R. Netter, *Compt. rend.,* **189**, 299 (1929)].

(4) (a) A. H. Blatt. "Organic Syntheses." Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1944. p. 205; (b) F. J. Pond, H. J. York and B. L. Moore, THIS JOURNAL, **23**, 790 (1901); (c) R. D. Abell. *J. Chem. Soc.,* **101**, 1000 (1912).

tained in a yield of 95% and it was found to consist of about 66% of the *trans*-isomer and 34% of an oil which has now been characterized and is here designated as the *cis*-isomer. Benzoylphenylacetylene[5a] apparently was not formed to any significant extent. When the lower-melting dibromide was dehydrohalogenated similarly by the action of potassium acetate, reaction occurred much more rapidly and an 87% yield of product was obtained which proved to be nearly pure crystalline *trans*-isomer. Both *cis*- and *trans*-α-bromobenzalacetophenones were shown in separate experiments to be stable under these reaction conditions and therefore were independent products. Although the dehydrohalogenations had not followed fully consistent stereochemical courses, there was exhibited significantly different behaviors of the two dibromides.

The new (*cis*) isomer has been obtained directly by sunlight inversion of an isoöctane solution of the crystalline (*trans*) isomer. It is a yellow oil which in spite of its lability and the difficulty of purification by ordinary techniques has been obtained in a relatively high state of purity (*ca.* 96–97%). The sunlight inversion from *trans* to *cis* was practically complete, and the position of the photoequilibrium appeared to lie far over on the side of the *cis* isomer. The conversion of the new (*cis*) isomer back into the solid (*trans*) isomer was brought about (a) by heating at 160°, (b) by the action of iodine under heating at 100°, and (c) by the action of sunlight on a chloroform solution containing iodine. These reactions show that the solid (*trans*) isomer actually is the stable form and that the new (*cis*) isomer is the labile form. Since steric interference between spatially adjacent

(5a) *Cf.* C. L. Bickel, THIS JOURNAL. **69**, 2134 (1947); **72**, 349 (1950).