Somewhat strangely, VII was also recovered in substantial amounts from the reactions of I with both *t*-butylmagnesium bromide and cyclohexylmagnesium bromide. It is most probable that VII was derived from 2 moles of isocyanate, but the Grignard reagent is apparently necessary to bring this about. Table I summarizes the results of the reactions of I with various Grignard reagents.

TABLE I

$$\underset{\text{I}}{C_6H_5CONCO} + RMgX \longrightarrow \underset{\text{II}}{C_6H_5CONHCOR} + \underset{\text{III}}{C_6H_5COR} + \underset{\text{IV}}{C_6H_5CONHCONHCOC_6H_5} + \underset{\text{V}}{C_6H_5CONHCONH_2} + \underset{\text{VI}}{C_6H_5CONH_2} + \underset{\text{VII}}{C_6H_5CONHCOC_6H_5}$$

R	Yield of products, % II	III	IV	V	VI	VII
CH_3 (f)[a]		23.6	32.0			
CH_3 (r)[a]		5.0	32.7			
C_2H_5 (f)		26.1	38.5		6.0	
C_2H_5 (r)		6.8	24.6			
$(CH_3)_2CH$ (f)			50.9			
$(CH_3)_2CH$ (r)	52.3			20.0		
$(CH_3)_3C$ (f)			8.0	20.0		30.0
$(CH_3)_3C$ (r)			45.2			31.3
C_6H_{11} (f)		19.3	49.0			Trace
C_6H_{11} (r)		2.0	14.9			48.9
C_6H_5 (f)		15.0	79.0		4.0	
C_6H_5 (r)	79.0[b]	3.5			9.2	79.0[b]
o-$CH_3OC_6H_4$ (f)	3.5		25.7			
o-$CH_3OC_6H_4$ (r)	14.4		27.4			
p-$CH_3C_6H_4$ (f)			69.3			
p-$CH_3C_6H_4$ (r)	22.1		6.0			

[a] Forward addition is indicated by f and r denotes reverse addition. [b] In this case II and VII are the same.

Experimental Section

Benzoylisocyanate (I) was prepared according to the procedure of Arcus and Prydal.[5] Ether was dried over sodium before use. The halides used were all commercial products. The experiments below typify the techniques used with all Grignard reagents.

Reaction of I with Phenylmagnesium Bromide. A. Forward Addition.—Phenylmagnesium bromide was prepared with 7.63 g (0.0486 mole) of bromobenzene and 1.06 g (0.0436 g-atom) of magnesium in 50 ml of ether. To the Grignard reagent was added with stirring under N_2 5.96 g (0.0406 mole) of I in 30 ml of ether at room temperature during 20 min. After stirring for 2 hr, the mixture was hydrolyzed with 100 ml of 1 *N* HCl and during hydrolysis 4.30 g (79.0%) of N,N′-dibenzoylurea (IV) precipitated, mp 180–190°. Recrystallization from toluene and from $CHCl_3$ gave IV with constant mp 213–214°; with authentic IV, mmp 214–215°.

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.16; H, 4.48; N, 10.45. Found: C, 67.16; H, 4.78; N, 10.34.

Work-up of the ether layer gave a thick oil. The use of vpc (column of 5% SF-96 60–80 Chromosorb G) at 200° showed the oil to contain a 15.0% yield of benzophenone (III), and a 4.0% yield of benzamide (VI). Further confirmation of III was obtained by preparing the 2,4-dinitrophenylhydrazone, mp 238–240°; with the derivative from authentic III, mmp 239–240°.

The addition of I to 3 moles of Grignard reagent under the above conditions gave an oil. Analysis by vpc showed 60.6 and 13.4% yields, respectively, of III and VI, along with other unidentified materials.

B. Reverse Addition.—Grignard reagent prepared from 5.12 g (0.0326 mole) of bromobenzene and 0.769 g (0.0316 mole g-atom) of magnesium in 45 ml of ether was added during 15 min at room temperature to 4.59 g (0.0312 mole) of I in 20 ml of ether. The reaction mixture was stirred vigorously for 2 hr at room temperature and hydrolyzed as above. During hydrolysis 5.40 g (77.0%) of solid precipitated, mp 137–144°. Another 0.14 g (2.0%) of similar material was obtained from work-up of the ether layer. Recrystallization from benzene gave N-benzoylbenzamide (VII) with a constant melting point of 149–150° (lit.[6] mp 148°).

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.67; H, 4.89; N, 6.22. Found: C, 74.60; H, 4.99; N, 6.04.

An independent synthesis of VII was effected by the method of Titherley,[6] mp 148–149°; with VII above, mmp 148–149°. The infrared spectrum of VII showed bands at 3350, 1700, and 1675 cm^{-1}. The nmr spectrum showed an NH band at τ 0.75 and aromatic hydrogens in the 2.18–2.50 range.

Analysis of the oil residue from the reaction by vpc and by the use of 2,4-dinitrophenylhydrazine gave a 3.5% yield of III and a 9.2% yield of VI.

Registry No.—I, 4461-33-0; VII, 614-28-8.

---

(5) C. L. Arcus and B. S. Prydal, *J. Chem. Soc.*, 4018 (1954).

(6) A. W. Titherley, *ibid.*, **85**, 1684 (1904).

The Reaction of Potassium Cyanide with *p*-Phenylsulfonylbenzyl Bromide

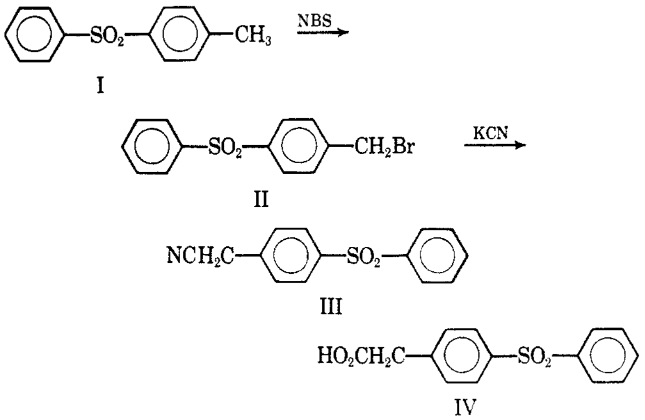
F. J. LOTSPEICH

Department of Biochemistry, West Virginia University Medical Center, Morgantown, West Virginia

Received June 20, 1966

During the course of our studies on vitamin A esters, we were interested in preparing *p*-phenylsulfonylphenylacetic acid (IV) for use as a possible "handle" in the purifications of vitamin A. Initially the preparation of this acid was attempted according to Scheme I.

SCHEME I



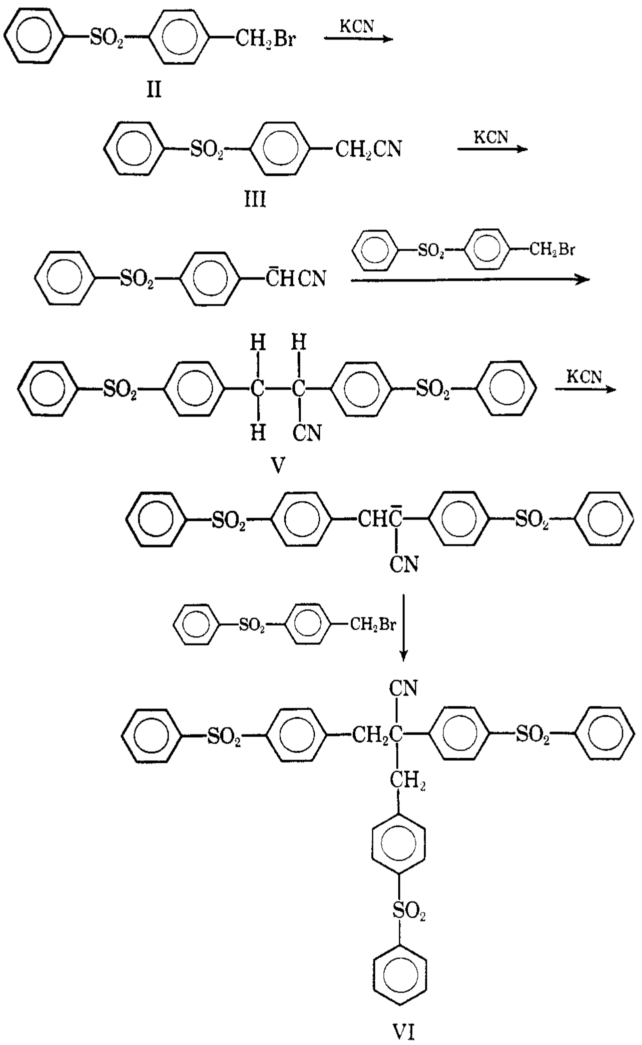
The bromination of *p*-phenylsulfonyltoluene (I) with N-bromosuccinimide proceeded smoothly resulting in a high yield of brominated product. However, this product could not be successfully purified by crystallization or column chromatography over aluminum oxide. The bromination product yielded a solid devoid of halogen when treated with methanolic alkali. The hydrolyzed material could not be crystallized to a sharp melting point and the infrared spectrum showed no evidence of a carbonyl or hydroxyl band. However, the infrared spectrum did exhibit an absorption band at 1101 cm^{-1} indicating the presence of an ether linkage. Evidently the reactivity of the halogens was such that ether formation[1] occurred before hydrolysis. When the material was hydrolyzed in boiling water for 24 hr a solid was obtained which still resisted purification by crystallization. However, in this case absorption bands in the infrared at 3533 and 1699 cm^{-1} supported the presence of a hydroxyl and a carbonyl group. The 2,4-dinitrophenylhydrazone prepared from the mixture showed a correct analysis for the 2,4-dinitrophenylhydrazone of *p*-phenylsulfonylbenzaldehyde. Based on the infrared spectrum of the hydrolyzed brominated mixture and the amount of 2,4-dinitrophenylhydrazone present, the reaction mixture was composed of approximately 80% *p*-phenylsulfonylbenzyl bromide (II) and 10% of *p*-phenylsulfonylbenzal bromide.

The preparation of pure *p*-phenylsulfonylbenzyl bromide (II) was successfully achieved by the reduction of *p*-phenylsulfonylbenzoyl chloride with lithium aluminum hydride followed by treatment of the resulting *p*-phenylsulfonylbenzyl alcohol with phosphorus tribromide. When *p*-phenylsulfonylbenzyl bromide (II) was added to a solution of potassium cyanide in aqueous acetone a lemon yellow color formed instantaneously and a solid slowly precipitated. This precipitate was sparingly soluble in most organic solvents at room temperature and contained nitrogen but no halogen. The absorption of the nitrile group usually found between 2200 and 2300 cm^{-1} was not present in the spectrum of this compound. However, this evidence did not necessarily rule out the presence of the nitrile group since Bellamy[2] indicates that the absorption of the nitrile group in the infrared is considerably reduced and quite often missing in compounds which contain oxygen. Since the cyanide ion is a strong base as well as a good nucleophilic ion it was possible that *p,p'*-diphenylsulfonylstilbene was formed in a manner similar to the formation of *p,p'*-dinitrostilbene reported by Friedman and Schechter.[3] In this particular case the dinitrostilbene was formed in 70% yield when *p*-nitrobenzyl chloride was treated with sodium cyanide in dimethyl sulfoxide at 35–40°. Hauser, *et al.*,[4] also reported the formation of stilbene when benzyl chloride was treated with sodium amide in liquid ammonia.

If *p*-phenylsulfonylbenzyl bromide (II) were undergoing a reaction similar to that reported by Friedman or Hauser, then a base such as potassium hydroxide might be expected to bring about a similar reaction. However, potassium hydroxide did not produce a yellow color or a precipitate under similar experimental conditions and it thus appeared that the explanation involved more than the initial formation of the anion of *p*-phenylsulfonylbenzyl bromide (II).

The extremely rapid reaction of *p*-phenylsulfonylbenzyl bromide (II) with sodium iodide in acetone suggested the possibility that the cyanide ion initially displaced the bromide ion and thus activated the methylene group which then reacted according to Scheme II. Hauser, *et al.*,[5] recently reported a similar reaction where phenylacetonitrile was alkylated with various halides in the presence of base.

Scheme II



To test this possibility methyl *p*-phenylsulfonylphenylacetate which has an active methylene group similar to that of *p*-phenylsulfonylphenylacetonitrile (III) was prepared by the Arndt–Eister method.[6] *p*-Phenylsulfonylbenzoyl chloride was treated with diazomethane and the resulting diazo ketone was converted to the acid by treatment with silver oxide. The acid was converted to the methyl ester by treatment with phosphorus pentachloride and then methanol. When this ester was treated with potassium hydroxide in acetone, a lemon yellow color immediately appeared. The color disappeared when *p*-phenylsulfonylbenzyl bromide (II) was added to the acetone solution. Evaporation of the acetone yielded a solid devoid of halogen which melted at 194.5–196° and showed a correct analysis for methyl 2,3-di(*p*-phenylsulfonylphenyl)-propionate.

The experimental evidence presented strongly suggests that *p*-phenylsulfonylbenzyl bromide (II) reacts initially with potassium cyanide in acetone to yield the expected compound, *p*-phenylsulfonylphenylacetonitrile (III). However, this compound which now contains extremely reactive methylene hydrogens forms an anion and reacts with additional *p*-phenylsulfonyl-

---

(1) N. T. Farinacci and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 2542 (1937).

(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p 266.

(3) L. Friedman and H. Schechter, *J. Org. Chem.*, **25**, 877 (1960).

(4) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *J. Am. Chem. Soc.*, **78**, 1653 (1956).

(5) W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *J. Org. Chem.*, **30**, 4135 (1965).

(6) W. E. Bachman and W. S. Struve, *Org. Reactions*, **1**, 51 (1947).

benzyl bromide to yield 2,2-di(*p*-phenylsulfonylbenzyl)-*p*-phenylsulfonylphenylacetonitrile (VI).

Experimental Section

Melting points were taken using a Nalge–Axelrod melting point apparatus and are uncorrected. *p*-Phenylsulfonyltoluene, *p*-phenylsulfonylbenzoic acid, and *p*-phenylsulfonylbenzoyl chloride were prepared according to the procedure of Newell.[7]

***p*-Phenylsulfonylbenzyl Alcohol.**—*p*-Phenylsulfonylbenzoyl chloride (10.0 g, 0.0356 mole) dissolved in the minimum amount of dry dioxane was added dropwise to a stirred solution of 3.00 g (0.0791 mole) of lithium aluminum hydride in 300 ml of anhydrous diethyl ether. The reaction mixture was stirred for 2 hr. and then decomposed by the dropwise addition of water. The solution was acidified with hydrochloric acid and the ether layer separated. The aqueous solution was extracted with two 50-ml portions of diethyl ether and the ether extracts were combined and dried. The solid (5.57 g, 63%) remaining after evaporation of the ether melted at 135–137° after recrystallization from methanol.

Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.88; H, 4.87. Found: C, 63.00; H, 5.15.

***p*-Phenylsulfonylbenzyl Bromide (II).**—*p*-Phenylsulfonyltoluene (5.00 g, 0.0215 mole), 3.92 g (0.0220 mole) of N-bromosuccinimide, and 0.25 g of benzoyl peroxide were added to 400 ml of carbon tetrachloride and refluxed for 18 hr. The carbon tetrachloride was evaporated and the remaining solid was washed with dilute, aqueous sodium thiosulfate and water. The solid residue (6.5 g) was air dried and recrystallized from benzene and hexane to a melting point of 100–110°. Repeated recrystallization from cyclohexane, aqueous acetone, dioxane, and ethyl acetate raised the melting point to 120–130° but a sharper melting point could not be obtained.

One gram of the solid residue was dissolved in the minimum amount of benzene and placed on an aluminum oxide (Merck) column (2 × 18 mm) prepared in benzene. The column was eluted with benzene–hexane (15:85) and then hexane. Five-milliliter fractions were collected. None of the fractions had sharp melting points and the melting points could not be improved by further recrystallization.

p-Phenylsulfonylbenzyl alcohol (5.00 g, 0.0201 mole) and 10.0 g (0.00369 mole) of phosphorus tribromide were allowed to stand for 24 hr. The resulting material was decomposed with ice water and washed with cold 2% aqueous sodium bicarbonate and water. The dry solid (5.6 g, 89%) melted at 137–139° after recrystallization from benzene and petroleum ether (bp 37°).

Anal. Calcd for $C_{13}H_{11}BrO_2S$: C, 50.17; H, 3.56. Found: C, 50.59; H, 3.63.

The Reaction of *p*-Phenylsulfonylbenzyl Bromide (II) with Potassium Cyanide.—Potassium cyanide (0.22 g, 0.0034 mole) was dissolved in 50 ml of acetone and 4 ml of water. *p*-Phenylsulfonylbenzyl bromide (1.00 g, 0.00321 mole) was added and the immediate formation of a yellow color was noted. At the end of 4 hr the white precipitate was filtered, washed with water, and recrystallized from dioxane. The resulting solid (VI, 0.55 g, 72%) melted at 262–265°. The material contained no halogen but did contain nitrogen. The solid was sparingly soluble or insoluble in benzene, methanol, hexane, diethyl ether, and chloroform at room temperature.

Anal. Calcd for $C_{40}H_{31}NO_6S_3$: C, 66.92; H, 4.35, mol wt, 718. Found: C, 66.62; H, 4.25; mol wt, 735.

***p*-Phenylsulfonylphenylacetic Acid (IV).**—*p*-Phenylsulfonylbenzoyl chloride (6.70 g, 0.0239 mole) dissolved in 100 ml of dioxane was added dropwise at 5–10° to a solution of diazomethane prepared from 24 g of N-methyl-N-nitroso-*p*-toluenesulfonamide in 150 ml of diethyl ether. After 4 hr at 10° and 8 hr at room temperature the solvent was removed under vacuum and the resulting *p*-phenylsulfonylbenzoyldiazomethane (5.00 g, 73%) was recrystallized from benzene; mp 140–142°.

p-Phenylsulfonylbenzoyldiazomethane (5.00 g, 0.0175 mole) dissolved in 60 ml of dioxane was slowly added to 6.0 g of freshly prepared silver oxide suspended in 250 ml of water containing 8.0 g of sodium carbonate. The temperature was maintained at 50–60° during the addition and then raised to 95° for 1 hr after the addition was complete. The solution was cooled and filtered. The light orange filtrate was acidified with dilute nitric acid and extracted with diethyl ether. The extract was washed with water and evaporated to yield 3.6 g (74%) of solid (IV) which, after recrystallization from benzene and then dichloromethane, melted at 128–230°.

Anal. Calcd for $C_{14}H_{12}O_4S$: C, 60.85; H, 4.38. Found: C, 60.48; H, 4.30.

Methyl *p*-Phenylsulfonylphenylacetate.—*p*-Phenylsulfonylphenylacetic acid (IV) (2.00 g, 0.00724 mole) was added to 50 ml of carbon disulfide followed by 1.51 g (0.00725 mole) of phosphorus pentachloride. The mixture was allowed to stand at room temperature for 12 hr. The carbon disulfide and phosphorus oxychloride were removed under vacuum and 100 ml of anhydrous methanol was added to the impure acid chloride. The solution was allowed to stand for 8 hr and the methanol was then removed under vacuum. The resulting solid (1.81 g, 86%) was recrystallized from aqueous methanol, mp 68–70°.

Anal. Calcd for $C_{15}H_{14}O_4S$: C, 62.05; H, 4.86. Found: C, 61.90; H, 4.68.

Methyl 2,3-Di(*p*-phenylsulfonylphenyl)propionate.—Potassium hydroxide (0.200 g, 0.00356 mole) was dissolved in 50 ml of acetone and a minimum amount of water. When methyl *p*-phenylsulfonylphenylacetate (1.00 g, 0.00344 mole) was added to the solution a lemon yellow color developed which instantaneously disappeared when 1.08 g (0.00347 mole) of *p*-phenylsulfonylbenzyl bromide was added. The solution was allowed to stand 2 hr and the acetone was evaporated. The resulting solid (1.44 g, 80%) was recrystallized from methanol and dichloromethane to yield white crystals (mp 194.5–196°).

Anal. Calcd for $C_{28}H_{24}O_6S_2$: C, 64.60; H, 4.64; mol wt, 522. Found: C, 64.50; H, 4.59; mol wt, 510 (Rast).

***p*-Phenylsulfonylbenzyl Iodide.**—*p*-Phenylsulfonylbenzyl bromide (5.00 g, 0.0161 mole) dissolved in 50 ml of acetone was treated at room temperature with 2.40 g (0.0160 mole) of sodium iodide dissolved in 20 ml of acetone. The precipitation of sodium bromide began immediately. After 1 hr the sodium bromide was filtered and the acetone was evaporated to yield reddish crystals. These crystals were dissolved in hot benzene and treated with Norit. Addition of petroleum ether (bp 37°) to the benzene solution followed by slow cooling yielded 5.21 g (91%) of white crystals, mp 129–132°. These crystals tended to decompose on standing at room temperature, and this is probably responsible for the discrepancy noted in the analysis.

Anal. Calcd for $C_{13}H_{11}O_2SI$: C, 43.59; H, 3.10. Found: C, 44.10; H, 3.20.

Hydrolysis of Impure *p*-Phenylsulfonylbenzyl Bromide.—Impure *p*-phenylsulfonylbenzyl bromide (2.00 g) was dissolved in 100 ml of methanol containing 1.00 g of potassium hydroxide and 5 ml of water. The solution was refluxed for 1 hr and the methanol was evaporated by means of an air jet. The resulting solid was washed with water and recrystallized from aqueous methanol and then hexane, mp 85–94°. Repeated recrystallization of the material from aqueous methanol raised the melting point to 90–95°. These crystals give a negative Beilstein test and had an infrared band at 1101 cm^{-1}.

The product (2.00 g) from the N-bromosuccinimide reaction was stirred vigorously with 800 ml of boiling water for 36 hr. The hot solution was then filtered rapidly and allowed to cool. The resulting white crystals (1.2 g) gave a negative Beilstein test. These crystals were insoluble in 5% sodium bicarbonate and could not be crystallized to a sharp melting point. The infrared spectrum of the solid exhibited a band at 3533 and 1699 cm^{-1}.

The 2,4-dinitrophenylhydrazone prepared from the mixture and recrystallized from methanol melted at 260–270°.

Anal. Calcd for $C_{19}H_{14}N_4O_6S$: C, 53.52; H, 3.31. Found: C, 53.10; H, 3.49.

***p*-Phenylsulfonylbenzyl Methyl Ether.**—*p*-Phenylsulfonylbenzyl bromide (2.00 g, 0.00643 mole) was refluxed for 1 hr with 100 ml of methanol containing 0.2 g of potassium hydroxide and 2 ml of water. The methanol was evaporated and the resulting solid was washed with water and recrystallized from methanol. The resulting white crystals (1.52 g, 90%) melted at 95–97°.

Anal. Calcd for $C_{14}H_{14}O_3S$: C, 64.09; H, 5.38. Found: C, 63.74; H, 5.25.

Registry No.—II, 7705-63-7; *p*-phenylsulfonylbenzyl alcohol, 7705-64-8; VI, 7705-65-9; IV, 7721-90-6; methyl *p*-phenylsulfonylphenylacetate, 7705-66-0; methyl 2,3-

---

[7] L. C. Newell, *Am. Chem. J.*, **20**, 302 (1898).

di(*p*-phenylsulfonylphenyl)propionate, 7705-67-1; *p*-phenylsulfonylbenzyl iodide, 7718-66-3; *p*-phenylsulfonylbenzyl methyl ether, 7705-68-2.

Reactions of Aromatic Solids with Halogen Vapors

M. M. LABES AND H. W. BLAKESLEE

Chemistry Division, The Franklin Institute Research Laboratories, Philadelphia, Pennsylvania 19103, and the Department of Chemistry, Drexel Institute of Technology, Philadelphia, Pennsylvania 19104

Received November 18, 1966

In a recent study of the decomposition of perylene–bromine charge-transfer complex in the solid state, 3,9-dibromoperylene with no trace of monobromo or other dibromo derivatives was formed when the reaction was conducted at temperatures below −9°.[1] There are only a few other examples of the use of solid-state forces to control isomer distribution or stereochemistry in an organic reaction. Prelog, *et al.*,[2] observed the spontaneous decomposition of cyclodecyltosylate in the solid state to lead exclusively to *cis*-cyclodecene while the reaction in the liquid phase (acetolysis) yields 20% *cis* and 80% *trans*. Photodimerizations in solids sometimes reflect the geometric consequences of the crystal lattice.[3] Kornblum and Lurie[4] report that when sodium and potassium phenoxides are alkylated heterogeneously, carbon alkylation occurs, whereas the reaction in homogeneous solution gives exclusively oxygen alkylation. They argue that for O alkylation to occur, a linear transition state with a negative charge originally present on oxygen progressively being transferred to halogen is involved; in the solid this is improbable since loss of the charge on oxygen would give rise to strong electrostatic repulsion between the sodium ions which cannot move away from one another in the solid lattice. C alkylation, on the other hand, involves a transition state in which sodium ion nestles between oxygen and halogen atoms, a much more satisfactory geometry.

Bromination of solid anthracene was noted in 1870.[5] The precise conditions were not defined, but presumably the reaction was conducted in the light at room temperature by exposing anthracene powder to bromine vapor. The β form of 9,10-dibromo-1,2,3,4-tetrabromotetrahydroanthracene was said to form. Buckles, *et al.*,[6] studied a large group of aromatic compounds under conditions in which the reaction undoubtedly occurred in a film of solution on the surface of the solid. Our earlier work[1] gave some qualitative observations on the exposure of hydrocarbon films to bromine.

The question which motivated this investigation was to what extent can crystal forces exercise control of isomer distribution in a gas–solid reaction? Accordingly, the chlorination of acetanilide, chlorination and bromination of sodium phenoxide, and photochlorination of benzene in the solid state were examined and the isomer distribution of the products was analyzed.

Many reaction systems were screened in an attempt to find cases where no appreciable vapor pressure of the solid reactant existed or no liquefaction occurred upon condensing reacting quantities of the gas on the solid substrate. The systems studied represent attempts to minimize these possibilities by utilizing primarily high melting point substrates and low reaction temperatures. No macroscopic liquefaction was observed, but a liquid phase existing at the surface can not be rigorously excluded. It was hoped that a charge-transfer complex of some aromatic compounds could be prepared in this way, analogous to the formation of perylene–bromine or condensed aromatic hydrocarbon–iodine complexes. No evidence could be found to indicate that a discrete complex could be prepared *via* a gas–solid interaction for the three compounds studied here in detail; all of the halogen could be removed without reaction occurring by continual pumping at very low temperatures and no visible color changes occurred. The formation of CT complex of benzene–chlorine has been reported;[7] evidently, it is sufficiently unstable to be readily dissociated upon pumping at −196°. In all the cases studied, the reaction was conducted at the lowest temperatures at which a reasonable rate prevailed.

The results of the studies of gas–solid halogenations are presented in Table I. The ratios of *ortho* and *para* isomers obtained in this work can be compared with the typical isomer distributions in homogeneous solutions employing molecular halogens and show remarkable agreement. There appears to be little or no effect of crystal forces in these cases on the course of the reaction. Yields are quite high because the surface/volume ratio of the materials is also high.

It was of interest to examine whether the isomer distribution in such a solid–gas reaction varied with per cent reaction. Certainly during the initial portion of the reaction when little or no product has been formed, there is less danger of liquefaction occurring and confusing the results. Table II presents the results of such a study of the chlorination of acetanilide.

Although the results during the short reaction times are not very accurate, there does not appear to be any control of isomer distribution during the early phases of the reaction. The results of Kornblum and Lurie[4] in the heterogeneous reaction of benzyl chloride with potassium *p*-*t*-octylphenoxide in toluene at 25° were as follows: at 4% completion, there was no O benzylation and exclusively C; at 16% the O–C alkylation ratio was 5:95; and at 100% it was 86:14. This is the only nonphotochemical case we are aware of in which lattice control of product occurs during a surface reaction.

Thus it appears that reactions which occur in the bulk, such as a unimolecular decomposition or the de-

---

(1) M. M. Labes, H. W. Blakeslee, and J. E. Bloor, *J. Am. Chem. Soc.*, **87**, 4251 (1965).

(2) V. Prelog, W. Kung, and T. Tomljenovic, *Helv. Chim. Acta*, **45**, 1352 (1962).

(3) For a review of photochemical reactions in the organic solid state, see H. S. A. Gilmour, "Physics and Chemistry of the Organic Solid State," Vol. I, D. Fox, M. M. Labes, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 329.

(4) N. J. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, **81**, 2705 (1959).

(5) C. Graebe and C. Liebermann, *Ann. Suppl.*, **7**, 257 (1870).

(6) R. E. Buckles, E. A. Hausman, and N. G. Wheeler, *J. Am. Chem. Soc.*, **72**, 2494 (1950).

(7) O. Hassel and H. Stromme, *Acta Chem. Scand.*, **13**, 1781 (1959).