C_8H_9NOS: C, 57.46; H, 5.42; N, 8.38; S, 19.17. Found: C, 57.20; H, 5.35, N, 8.10; S, 18.98.

***N*-[[(Carboethoxy)methyl]thio]acetamide.** NMR δ 8.2 (1 H, s), 4.2 (2 H, q), 3.5 (2 H, s), 2.2 (3 H, s), 1.3 (3 H, t). IR 3150 (N-H), 1730 (-C(O)O-), 1670 (C=O) cm^{-1}. Exact mass: calcd for $C_6H_{11}NO_3S$, 177.0460; found, 177.0459.

***N*-(Benzylthio)acetamide.** NMR δ 7.2 (5 H, s), 3.85 (2 H, s), 1.9 (3 H, s). IR 3240 (N-H), 1660 (C=O) cm^{-1}. Anal. Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.12; N, 7.73. Found: C, 59.78; H, 6.33; N, 7.59.

***N*-(*p*-Tolylthio)acetamide.** NMR δ 7.1 (4 H, s), 2.35 (3 H, s), 2.1 (3 H, s). IR 3195 (N-H), 1675 (C=O) cm^{-1}. Anal. Calcd for $C_9H_{11}NOS$: C, 59.64; H, 6.12; N, 7.73. Found: C, 59.76; H, 6.39; N, 7.54.

***N*-[(*o*-Nitrophenyl)thio]acetamide.** NMR δ 7.1-8 (4 H, m), 2.1 (3 H, s). IR 3200 (N-H), 1665 (C=O), 1330 (NO_2) cm^{-1}. Anal. Calcd for $C_8H_8NO_3S$: C, 45.27; H, 3.80; N, 13.20. Found: C, 45.42; H, 3.91; N, 13.07.

***N*-Sulfinylacetamide.** To a solution of the *N*-(thio)acetamide (20 mmol) in 100 mL of $CHCl_3$ at 0 °C was added dropwise over 1 h a solution of *m*-chloroperbenzoic acid (20 mmol) in 40 mL of $CHCl_3$. The reaction was stirred for a further 0.5 h and then evaporated. Addition of ether to dissolve *m*-chlorobenzoic acid followed by filtration afforded the *N*-sulfinylacetamide in 80% yield.

***N*-(Phenylsulfinyl)acetamide.** NMR δ 7.6 (5 H, s), 2.0 (3 H, s). IR 3000 (N-H), 1670 (C=O), 1050 (S=O) cm^{-1}. Exact mass: calcd for $C_8H_9NO_2S$, 183.0354; found, 183.0374. Yield 82%; mp 105-108 °C.

***N*-[[(Carboethoxy)methyl]sulfinyl]acetamide.** NMR δ 4.3 (2 H, q), 4.0 (2 H, s), 2.2 (3 H, s), 1.3 (3 H, t). IR 3200 (N-H), 1720 (-C(O)O-), 1680 (C=O), 1070 (S=O) cm^{-1}. Exact mass: calcd for $C_6H_{11}NO_4S$, 193.0409; found, 193.0414. Yield 73%; mp 66-68 °C.

Preparation of *N*-Bis(*p*-tolylthio)acetamide (4). To *N*-(trimethylsilyl)acetamide (31.5 mmol) in 30 mL of hexane was added *p*-tolylsulfenyl chloride in 10 mL of hexane over 1 h. Further stirring for 1 h afforded 5.4 g of a white solid. This was dissolved in CH_2Cl_2, extracted with H_2O (dried with $MgSO_4$), and evaporated (precipitation with hexane) to afford 4.43 g of a white solid which was separated by chromatography on silica gel (CH_2Cl_2). Two fractions were obtained: **1c** (47%) followed by **4** [34%; mp 64-67 °C; NMR δ 7.0 (8 H, $A_2'B_2'$), 2.4 (3 H, s), 2.3 (6 H, s); IR 1700 (C=O) cm^{-1}]. A molecular peak at 303 is observed for **4**.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the Department of Education of Quebec for financial support.

Registry No. 1 (R = C_6H_5), 71032-76-3; 1 (R = $C_6H_5CH_2$), 71032-77-4; 1 (R = *p*-$CH_3C_6H_4$), 69189-02-2; 1 (R = *o*-$NO_2C_6H_4$), 70413-90-0; 1 (R = $EtOCOCH_2$), 71032-78-5; **3** (R = C_6H_5), 71050-18-5; **3** (R = $EtOCOCH_2$), 71032-79-6; **4**, 71032-80-9; *N*-(trimethylsilyl)acetamide, 13435-12-6; phenylsulfenyl chloride, 931-59-9; benzylsulfenyl chloride, 26826-81-3; *p*-tolylsulfenyl chloride, 933-00-6; *o*-nitrophenylsulfenyl chloride, 7669-54-7; carboethoxymethylsulfenyl chloride, 71032-81-0.

Action of Potassium Amide in Ammonia on Some Benzophenone Derivatives. Evidence That *o*-Bromophenyl Anions Partition between Aryne Formation and Protonation to Aryl Bromides[1]

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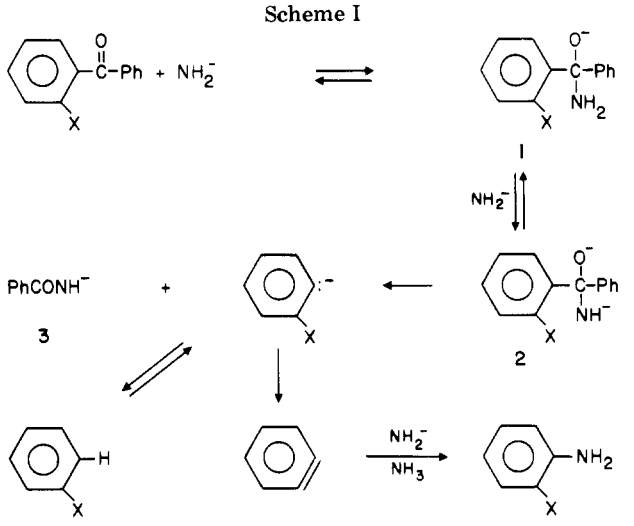
This research had two different but related objectives. One was to extend knowledge of the effects of substituents on the cleavage of benzophenones by KNH_2 in ammonia. Bunnett and Hrutfiord[3] observed that *o*-fluorobenzophenone is cleaved to form fluorobenzene, benzamide, and benzoic acid, that *o*-chlorobenzophenone furnishes aniline, benzamide, and benzoic acid, that *m*- and *p*-chlorobenzophenones furnish products in which the benzophenone framework remains intact with little or no cleavage, and that benzophenone itself is not cleaved. The mechanism of Scheme I was suggested for these reactions.[3] The initial work left unclear what effects other substituents would have on the occurrence of cleavage.

Scheme I



The second question was whether *o*-bromophenyl anions in ammonia solution are foreordained to lose bromide ion and form benzyne or whether they may at least in part take protons from the solvent to form bromobenzene molecules. In the pioneering work of Roberts and co-workers[4] on the aryne mechanism, it was found that the primary isotope effect, k_H/k_D, with respect to hydrogen in the 2-position of bromobenzene is 5.5 "which is close to the 6-7 range expected for a concerted E2 dehydrobromination".[4] Their conclusion that benzyne formation is concerted implies that *o*-bromophenyl anions formed in ammonia would react exclusively by bromide ion loss without being protonated at all by the solvent.

Results

Several substituted benzophenones were found to resist cleavage by KNH_2 in ammonia. They were the *m*-fluoro, *p*-fluoro, *o*-methoxy, and *p*-methoxy derivatives, as well as the anion of *o*-benzoylbenzoic acid. Probably these compounds did add amide ion, to form an adduct of the type shown on the first line of Scheme I, but such an adduct would decompose to regenerate the original benzophenone derivative during the conditions of workup employed.

o-Bromobenzophenone was cleaved to form benzamide (62%), benzoic acid (12%), and aniline (51%). That such cleavage would occur was implied by previous work[3] but not actually observed before.

2-Chloro-4-methylbenzophenone was cleaved by KNH_2 in ammonia to form benzamide (31%), benzoic acid (36%), and a mixture of isomeric toluidines (42%). The mixture of toluidines was acetylated, and the resulting acet-

(1) Based on the Sc.B. theses of D. S. Connor (1960) and K. J. O'Reilly (1962).
(2) University of California, Santa Cruz, CA 95064.
(3) Bunnett, J. F.; Hrutfiord, B. F. *J. Org. Chem.* **1962**, *27*, 4152.
(4) Roberts, J. D.; Semenow, D. A.; Simmons, H. E., Jr.; Carlsmith, L. A. *J. Am. Chem. Soc.* **1956**, *78*, 601.

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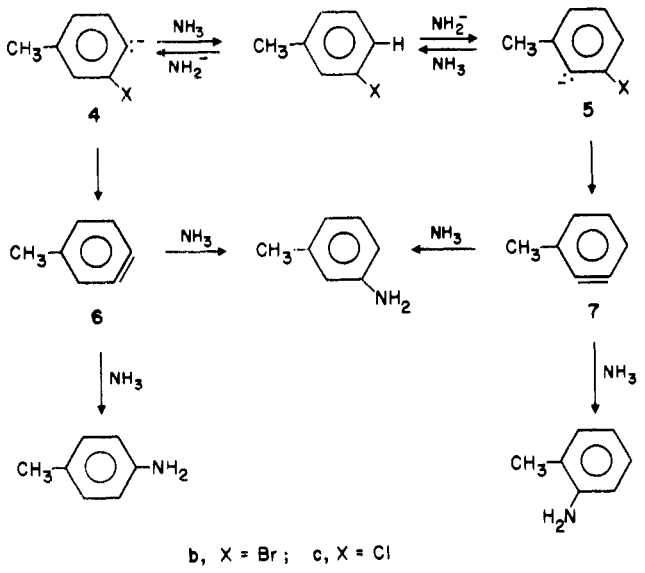
Scheme II



b, X = Br; c, X = Cl

toluidides were separated by liquid chromatography on alumina. The mixture was comprised of 28% of the ortho isomer, 65% of the meta isomer, and 7% of the para isomer.

2-Bromo-4-methylbenzophenone was similarly cleaved to form benzamide (29%), benzoic acid (34%), and a mixture of isomeric toluidines (38%). The mixture of toluidines was acetylated and the acetyl derivatives were similarly separated. The mixture was comprised of 19% of the ortho isomer, 68% of the meta isomer, and 13% of the para isomer.

Discussion

A simple generalization emerges from the present work and the previous study:[3] *o*-halobenzophenones are readily cleaved by KNH_2 in ammonia at reflux, but benzophenones without ortho halogen substituents are not cleaved. We add the proviso that further research involving other substituents may require some modification of this generalization.

As previously,[3] the facility of cleavage of *o*-halobenzophenones is ascribed to the comparative stability of *o*-halophenyl anions. There is abundant evidence that they are much more stable than the isomeric *m*- or *p*-halophenyl anions and are formed orders of magnitude faster.[5] The rate-limiting step in the mechanism of Scheme I is assuredly the scission of dianion **2**, and only when the aryl anion formed is relatively low in energy can scission occur under the conditions employed.[6]

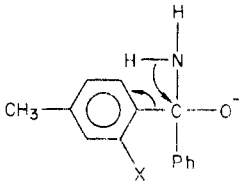
The cleavage of benzophenones by a reagent of KOH, potassium *tert*-butoxide, and *tert*-butyl alcohol in 1,2-dimethoxyethane is also assisted by an ortho halogen substituent. However, the conditions under which the most thorough study[8] of that type of benzophenone cleavage was conducted did not serve to single out the exceptionally favorable effect of ortho halogens. During 2–5 min at 20 °C, 2-chloro-, 3-chloro-, and 2-methoxybenzophenone and the anion of *o*-benzoylbenzoic acid were all cleaved virtually quantitatively, while benzophenone and several other derivatives required longer times and/or higher temperatures for substantial cleavage to occur.

The experiments with 2-chloro- and 2-bromo-4-methylbenzophenone are informative with respect to what happens to the *o*-halophenyl anion formed by the scission of **2**. We discuss this question with respect to Scheme II.

The aryl anion immediately formed by scission of a dianion of type **2** has structure **4**. If its only further reaction were loss of halide ion or if loss of halide ion were concerted with scission of the C–C bond, the only aryne formed would be **6**, and it would add ammonia to form a mixture of *m*- and *p*-toluidine without any *o*-toluidine. The fact that *o*-toluidine was formed in both cases points to the intermediacy of **7**. Given that the halogen was meta to methyl in the reactant benzophenones, aryne **7** must have been generated from carbanion **5** and it in turn from a *m*-halotoluene formed by protonation of **4**.

At least partial protonation of **4c** to form *m*-chlorotoluene would have been anticipated from the prior literature.[4,9] However, protonation of **4b** to *m*-bromotoluene would not. The present evidence that **4b** is at least in part protonated in liquid ammonia is novel and enlightening. We note that another study, performed more than 15 years after the present work was done, provides evidence to the same effect.[10]

In discussing the import of the fact that some *o*-toluidine is obtained from 2-chloro-4-methylbenzophenone, Bunnett and Hrutfiord[3] pointed out that if **1** were to undergo scission of the C–C bond concerted with proton transfer from nitrogen to carbon, as indicated by the arrows in transition state **8**, it would form *m*-chlorotoluene and the



8

conjugate base of benzamide directly and that in such a case the results would not be relevant to the behavior of **4c**. (Such a process would be much less likely in **2** because it would form the highly energetic dianion, $PhCON^{2-}$.) They commented that such a mechanism would not account for the specific activating effect of ortho halogen substituents but could not absolutely reject this possibility.

We now understand another and more severe difficulty with transition state **8**, namely, that it is a cyclic transition state involving movement of four electrons and therefore is antiaromatic.[11] It is objectionable on orbital-symmetry grounds. The many shortcomings of concerted scission via **8** warrant its rejection.

Roberts and co-workers[12] reported toluidine isomer proportions from the action of KNH_2 in ammonia on *m*-chlorotoluene to be 40% ortho, 52% meta, and 8% para and from *m*-bromotoluene to be 22% ortho, 56% meta, and 22% para, all figures to ±4%. They represented their determinations as qualitative but did not describe their method of analysis. In view of these uncertainties, we think little is to be gained from detailed comparison of their toluidine isomer proportions with those we deter-

(5) Bunnett, J. F. *Acc. Chem. Res.* **1972**, *5*, 139.
(6) An analogous scission of monoanion **1**, releasing benzamide instead of **3**, is conceivable. The kinetics of alkali cleavage of 2,6-dihalobenzaldehydes to formate ion and *m*-dihalobenzenes indicate that a doubly negative species analogous to **2** is what actually comes apart.[7] Scission of **2** is proposed by analogy.
(7) Bunnett, J. F.; Miles, J. H.; Nahabedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2512.
(8) Davies, D. G.; Derenberg, M.; Hodge, P. *J. Chem. Soc. C* **1971**, 455.
(9) Zoltewicz, J. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 2640.
(10) Bard, R. R.; Bunnett, J. F.; Traber, R. P., submitted for publication in *J. Org. Chem.*
(11) Perrin, C. L. *Chem. Br.* **1972**, *8*, 163.
(12) Roberts, J. D.; Vaughan, C. W.; Carlsmith, L. A.; Semenow, D. A. *J. Am. Chem. Soc.* **1956**, *78*, 611.

mined. They are broadly similar, and that may be taken as an indication that the rates of protonation of anions **4b** and **4c** (Scheme II) are relatively high as compared to the rates of halide ion loss to form aryne **6**.

Experimental Section

Materials. *p*-Methoxybenzophenone and *o*-benzoylbenzoic acid were commercial products whose identity was verified by melting point determination. 2-Chloro-4-methylbenzophenone was a sample prepared by Hrutfiord.[3] *p*-Fluorobenzophenone, mp 49.1–50.0 °C (lit.[13] mp 47–49 °C), was synthesized after McCarty et al. *o*-Methoxybenzophenone, mp 35.5–36.5 °C (lit.[14] mp 39 °C), was synthesized analogously by addition of *o*-methoxyphenylmagnesium bromide to benzonitrile and ensuing hydrolysis, in 50% yield. *o*-Bromobenzophenone, mp 29.2–29.6 °C, was synthesized in 78% yield by $AlCl_3$-catalyzed reaction of *o*-bromobenzoyl chloride with benzene.

m-Fluorobenzophenone was obtained in 70% yield by reaction of *m*-fluorobenzoyl chloride with a 2-mol proportion of $AlCl_3$ in excess benzene at reflux. The crude product was distilled at reduced pressure [bp 125–135 °C (12 mm)] and recrystallized from petroleum ether of bp 30–40 °C; mp 52.2–52.6 °C (lit.[15] mp 53 °C).

Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53. Found: C, 77.65; H, 4.45.

2-Bromo-4-methylbenzophenone was synthesized after DeTar and Relyea.[16] 2-Bromo-4-methylbenzoic acid, mp 150 °C, made by their method, was converted to its acid chloride by means of thionyl chloride, and the latter was combined with about a 1.8 molar proportion of $AlCl_3$ and heated at reflux in excess benzene for 3 h. The resulting 2-bromo-4-methylbenzophenone was crystallized from 95% ethanol; mp 41–42 °C.

Reactions of Benzophenone Derivatives with Potassium Amide. Reactions were conducted as previously described.[3] Four moles of KNH_2 were used per mole of ketone, and mixtures were in general held at reflux for 3 h before being quenched by addition of ammonium nitrate. However, when there was evidence of vigorous reaction in the form of strong boiling of the ammonia and strong color changes (as in all the cases in which cleavage occurred), the time of exposure was shorter, from 1 to 2 h. In some cases dry diethyl ether was present as a cosolvent, and in some such cases there were two liquid phases present. In several cases the starting benzophenone derivative was recovered from the reaction mixture and identified by melting point and mixture melting point in amounts as follows: *m*-fluorobenzophenone, 75%; *p*-fluorobenzophenone, 77%; *o*-methoxybenzophenone, 87%; *p*-methoxybenzophenone, 90%; *o*-benzoylbenzoic acid, 91%. From the cleavage of *o*-bromobenzophenone, benzoic acid (12%) and benzamide (62%) were identified by melting point and mixture melting point and aniline by comparison of its IR spectrum with that of an authentic sample.

The products of cleavage of 2-chloro- and 2-bromo-4-methylbenzophenone were separated into acidic, basic, and neutral fractions by extraction procedures. The acidic component was identified as benzoic acid by its melting point and mixture melting point. The neutral component was identified as benzamide by its melting point and mixture melting point. The basic fraction was an oil which was purified by distillation; bp 197 °C. Its infrared spectrum closely resembled that for a mixture of toluidine isomers.

Analysis of Toluidine Product Mixtures. One gram of each toluidine mixture was dissolved in 5% aqueous HCl. Dilute (5%) aqueous NaOH was added until the solution became permanently cloudy. Several drops of dilute HCl were then added until the cloudiness just disappeared, chips of ice were added, and then 5 mL of acetic anhydride was added. The solution was shaken vigorously, 5 g of sodium acetate in 25 mL of water was added, and agitation of the solution was continued for several minutes. The brownish precipitate which settled out upon chilling of the mixture was collected, air-dried, and placed on the alumina column to which solvent systems were applied. Elution with a mixture of 3:1 diethyl ether–chloroform removed aceto-*m*-toluidide. Elution with a mixture of equal parts of ether and chloroform then removed aceto-*p*-toluidide. Finally, the ortho isomer was removed by a mixture of 1:3 ether–chloroform. After evaporation of the solvent from each fraction collected, the fraction was weighed, its melting point and IR spectrum determined, and a mixture melting point determined with an authentic sample of the indicated acetotoluidide. Separation of the isomers was remarkably clean except that the first sample of the ortho isomer melted a little low in each case, specifically, 100 °C (from the chloro ketone) and 103.5 °C (from the bromo ketone) vs. 110 °C for pure aceto-*o*-toluidide; that means that the yields of ortho isomers are slightly overestimated at the expense of the para isomer.

Registry No. Aniline, 62-53-3; KNH_2, 17242-52-3; *o*-methoxyphenyl bromide, 578-57-4; benzonitrile, 100-47-0; *o*-bromobenzoyl chloride, 1711-09-7; benzene, 71-43-2; *m*-fluorobenzoyl chloride, 1711-07-5; 2-bromo-4-methylbenzoic acid, 7697-27-0; 2-bromo-4-methylbenzoyl chloride, 53456-09-0; *m*-fluorobenzophenone, 345-69-7; *p*-fluorobenzophenone, 345-83-5; *o*-methoxybenzophenone, 2553-04-0; *p*-methoxybenzophenone, 611-94-9; *o*-benzoylbenzoic acid, 85-52-9; *o*-bromobenzophenone, 13047-06-8; benzoic acid, 65-85-0; benzamide, 55-21-0; 2-chloro-4-methylbenzophenone, 71549-60-5; 2-bromo-4-methylbenzophenone, 69617-43-2; aceto-*m*-toluidide, 537-92-8; aceto-*p*-toluidide, 103-89-9; aceto-*o*-toluidide, 120-66-1.

(13) McCarty, F. J.; Tilford, C. H.; Van Campen, M. G., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 472.
(14) Stoermer, R.; Friderici, E. *Chem. Ber.* **1908**, *41*, 332.
(15) Moriconi, E. J.; O'Connor, W. F.; Forbes, W. F. *J. Am. Chem. Soc.* **1962**, *84*, 3928.
(16) DeTar, D. F.; Relyea, D. I. *J. Am. Chem. Soc.* **1956**, *78*, 4302.

Synthesis of 2-[2-Aryl-2-(*p*-toluenesulfonyl)ethyl]-1,3-dioxolanes

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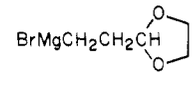
Umpolung of the intrinsic polarity of α,β-unsaturated aldehydes is presently achieved by two means. Acrolein, for example, is converted in one step into 2-(2-bromoethyl)-1,3-dioxolane which is then transformed into the Grignard derivative **1**. The terminal carbon atom hereby



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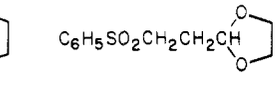

2

undergoes a changeover from an electrophilic to a nucleophilic center. The reagent has been used by Büchi in his synthesis of (±)-nuciferal[1] and by us as a synthon for constructing benzo[*b*]thiophenes,[2] benzimidazoles,[3] naphthalenes,[4] and 5-substituted butyrolactones.[5] A second approach makes use, in one way or another, of sulfur-stabilized carbanions,[6] the sulfur being brought on either the C-1 or the C-3 of the α,β-unsaturated aldehyde. Sulfones are especially practical in this strategy. This is illustrated by the three-step conversion of acrolein to 2-[(2-phenylsulfonyl)ethyl]-1,3-dioxolane (**2**) (C_6H_5SH addition, acetalization, and sulfur oxidation), whose corresponding anion was then both alkylated[7] and acylated.[8] The phenylsulfonyl group, having served its purpose, may later be removed by reduction or via β-elimination.[9]

Our continued interest in three-carbon homologation units plus specific research requirements for large amounts of varied 3-aryl-3-(arylsulfonyl)propionaldehydes made us look for practical means of preparing 2-[2-aryl-2-(*p*-toluenesulfonyl)ethyl]-1,3-dioxolanes **3a–d**. The present

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