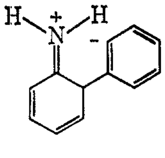
rate ratios for the three processes. In the formation of 2-aminobiphenyl from $C_6H_5NH_2$ and C_6H_4 a six-membered ring transition state is conceivable which would involve nucleophilic attack and protonation in one step, avoiding charge separation. In the formation of diphenylamine a four-membered ring transition state of this type is possible. In the formation of 4-aminobiphenyl no such cyclic transition state is possible. The fact that attack of the benzyne by $C_6H_5NH_2$ competes best with attack by C_6H_5NHK in the case of 2-aminobiphenyl formation and not at all in the case of 4-aminobiphenyl formation suggests that such a one-step cyclic process for the nucleophilic attack and protonation of benzyne by an amine is very probable.[8] Alternately, in a two-step process, the reaction of $C_6H_5NH_2$ and C_6H_4 to form 2-aminobiphenyl would lead to a charged intermediate having little charge separation, whereas the intermediate for 4-aminobiphenyl formation would involve a great deal of charge separation. This may account for the fact that no 4-aminobiphenyl at all could be found in the three much less polar solvents where such charge separation would be particularly energetically unfavorable.



It is of great interest that such simple changes in the steric and electrostatic nature of the transition states can so radically alter the degree of selectivity of benzyne between a pair of nucleophiles.

Experimental Section

Materials.—Aniline (Baker & Adamson) was dried over KOH and distilled from zinc dust. Bromobenzene (Baker) was dried over calcium sulfate and distilled. Dimethyl sulfoxide (Fisher Reagent) was dried over calcium hydride and distilled, ethyl ether and 1-4-1 were distilled from sodium wire.

Sample Run.—A mixture of potassium anilide and aniline (prepared from 4.75 g (0.510 mol) of aniline and 0.391 g (0.010 mol) of potassium) was dissolved in 50 ml of dimethyl sulfoxide. To this stirred solution was added 0.244 g (0.00155 mol) of bromobenzene and the solution left to stand at 25° under an atmosphere of nitrogen for 18 hr. The solution was then diluted with water and extracted with benzene. The benzene phase was washed thoroughly with water and then extracted with 3 *N* HCl. The organic phase, containing diphenylamine and triphenylamine, was then dried, an internal standard was added, and the mixture subjected to vpc analysis at 210° on a 5-ft long steel column packed with 20% SF-96 on 60/80 firebrick. The above aqueous HCl phase was neutralized with 10 *N* NaOH and extracted with ether. The ether phase, containing 2-aminobiphenyl and 4-aminobiphenyl, was then dried and analyzed by vpc as above. Samples of all four products were collected from the vpc and their infrared spectra determined. The spectrum of each compound was found to be identical with that of an authentic sample.

Registry No.—Benzyne, 462-80-6; bromobenzene, 108-86-1; potassium anilide, 19642-99-0; aniline, 62-53-3.

[8] A four-membered cyclic process of this type was proposed by Mack and Huisgen.[3] On the other hand, J. F. Bunnett, D. A. R. Happer, M. Patsch, C. Pyun, and H. Takayama [*J. Amer. Chem. Soc.*, **88**, 5250 (1966)] have good evidence for a stepwise addition of methanol to 4-chlorobenzyne in methanol solution.

Transannular Oxide Formation. Bicyclo[3.2.1] *vs.* Bicyclo[2.2.2] Systems

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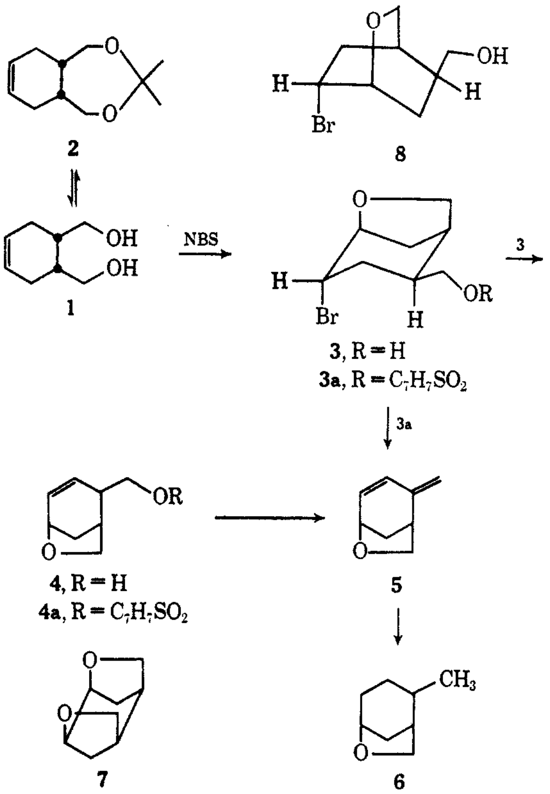
The relatively greater apparent stability of six-membered *vs.* five-membered oxide rings as evidenced, for example, by the preferred pyranose ring system in sugars as well as the formation of six-membered cyclic ketals in certain bicyclic systems[1] doubtlessly reflects the consequences of optimized conformational effects. In this connection it was of interest to us to determine the course of transannular oxide formation wherein competition exists for the formation of a bicyclo[3.2.1] or a bicyclo[2.2.2] product.

Treatment of the symmetrical system, *cis*-1,2-bishydroxymethylcyclohex-4-ene (1), with N-bromsuccinimide in aqueous *t*-butyl alcohol afforded a good yield of essentially a single bromoxide which proved to have the bicyclo[3.2.1] structure **3**[2] (Scheme I). The structure of **3** was established by conversion in essentially quantitative yield to a crystalline tosylate derivative **3a**, mp 80–81°; the latter, in turn, on treatment with

Scheme I



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[1] R. E. Beyler and L. H. Sarett, *J. Amer. Chem. Soc.*, **74**, 1406 (1952).

[2] Recently G. M. Brown, P. Dubrueil, and E. P. Denvers [*Can. J. Chem.*, **46**, 1849 (1968)] observed a similiar transannular oxide formation during epoxidation of a derived cyclohexene. The use of NBS in *t*-butyl alcohol for the formation of five-membered ring oxides has been previously reported. See, *e.g.*, F. W. Bollinger and N. L. Wendler, *Chem. Ind.* (London), 441 (1960); J. F. Bagl, P. F. Morand, and R. Gaudry, *J. Org. Chem.*, **28**, 1207 (1963).

potassium *t*-butoxide in ether was smoothly converted to the conjugated diene **5**, λ_{max} 238 mμ (ε 14,160). It may be noted that the bicyclo[2.2.2] structure **8** could not have provided a conjugated diene. Treatment of the bromoxide **3** itself with potassium *t*-butoxide yielded the olefinic alcohol **4** *in lieu* of the bisoxide **7**, again, presumably, for reasons of steric constraint (chair → boat) connoted in the latter system.

The diene **5** absorbed 2 moles of hydrogen to give the saturated system **6**. The unsaturated alcohol **4** in the form of its tosylate derivative **4a** was found to be stable to conditions employed for solvolysis of homoallylic systems, namely, potassium acetate in refluxing aqueous 80% acetone.[3] In the presence of potassium *t*-butoxide in ether suspension, on the other hand, **4a** was converted exothermically to the diene **5**.

Experimental Section

Vpc determinations were carried out employing a 5 ft × 0.25 in. 20% S.E. 30 on Chrom W Column. The uv spectrum was determined in methanol on a Cary Model II PMS spectrometer and ir spectra on a Perkin-Elmer Infracord instrument. Nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard.

1,2-Bishydroxymethylcyclohex-4-ene (1) was prepared by lithium aluminum hydride reduction of Δ^4-tetrahydrophthalic anhydride in ether–tetrahydrofuran solution and purified *via* its acetonide **2** (see below); lit.[4] bp 106–107° (1–1.5 mm) and mp 34.5°.

Acetonide of 1,2-Bishydroxymethylcyclohex-4-ene (2).—A solution of crude diol **1** (25 g) (see above) in 500 cc of acetone and 25 g of anhydrous copper sulfate was stirred for 18 hr followed by filtration and evaporation of the filtrate. The residue from concentration was extracted with petroleum ether (bp 30–60°) and the latter extract was washed several times with water, dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. Distillation of the residue, bp 60–61° (2 mm), afforded 18–20 g of acetonide **2**: single peak by vpc, 4-min retention time at 180°; nmr ($CDCl_3$), δ 1.3.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.82; H, 10.10.

Regeneration of diol **1** from acetonide **2** was effected by brief shaking with 10% hydrochloric acid and concentration *in vacuo* followed by treatment with sodium chloride and extraction with ether. Evaporation of the dried ($MgSO_4$) ether solution yielded diol **1** which was single peak by vpc with a retention time of 5.5 min at 180°.

Reaction of 1,2-Bishydroxymethylcyclohex-4-ene with N-Bromsuccinimide. Formation of Transannular Oxide 3.—A solution of 15.6 g of diol **1**, purified *via* its acetonide, in 165 cc of *t*-butyl alcohol and 33 cc of water was treated at 0–5° with 19.6 g of N-bromsuccinimide with stirring. The reaction mixture was allowed to stir until complete solution of the N-bromsuccinimide (*ca.* 1 hr) and stored for 16 hr in the refrigerator. Any excess positive bromine was destroyed with aqueous bisulfite and the reaction mixture was concentrated *in vacuo* to an oil. The latter was treated with water and extracted with ether. The ether extract was washed several times with water, dried over magnesium sulfate, filtered, and concentrated to give the bromoxide **3** as a colorless oil, 20 g, essentially single peak by vpc with a retention time of 7 min at 200°. This material is unstable to high-vacuum distillation and a sample for analysis was prepared by submitting a film to high vacuum for 18 hr.

Anal. Calcd for $C_8H_{13}O_2Br$: C, 43.44; H, 5.88; Br, 36.15. Found: C, 43.19; H, 5.86; Br, 36.15.

***p*-Toluenesulfonate 3a of Bromoxide.**—A 1.75-g sample of the above bromoxide **3** in 5 cc of pyridine was treated with 1.61 g of *p*-toluenesulfonyl chloride at 0° for 18 hr. The reaction mixture was treated with ice–water and the crystalline tosyl derivative was filtered, washed with water, and dried; 2.9 g, mp 74–76°, crystallization from ether gave mp 80–82°, ir of crude and crystallized material were the same.

Anal. Calcd for $C_{15}H_{19}SO_4Br$: C, 48.00; H, 5.07; Br, 21.33. Found: C, 48.12; H, 5.12; Br, 21.20.

Conversion of Tosylate 3a to Diene 5.—A solution of 650 mg of **3a** in 25 cc of ether was treated with 780 mg of potassium *t*-butoxide and stirred for 2 hr. At the end of this period water was added, the ether layer was separated and washed with water until neutral. Evaporation of the solvent yielded an oil exhibiting a single peak in the vpc with retention time of 1.5 min at 180°. The oil was evaporatively distilled at 75–80° (32 mm); λ_{max} 238 mμ (ε 14,160); λ_{max}^{film} 6.12, 6.28 μ; nmr, δ 4.69, 4.79 (each d, J = 1.5 cps, $>C{=}CH_2$), 6.05 (m, $CH{=}CH$).

Anal. Calcd for $C_8H_{10}O$: C, 78.69; H, 8.20. Found: C, 78.45; H, 8.48.

Hydrogenation of diene **5** (0.3 g) in 5 cc of ether employing 150 mg of 5% Pd–C catalyst resulted in absorption of 2 molar equiv of hydrogen and formation of the saturated analog **6** which was evaporatively distilled at 70° (32 mm), nmr, δ 0.85 (J = 6 cps, CH_3 doublet).

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.26; H, 11.11.

Reaction of Bromoxide 3 with Base to Give 4.—A solution of 1.7 g of bromoxide **3** in 15 cc of anhydrous ether was treated with 2 mole equiv of potassium *t*-butoxide. An exothermic reaction occurred which was allowed to continue with stirring at ambient temperature for 48 hr. The reaction mixture was treated with saturated salt solution and the ether extracts were washed with salt solution until neutral. Product distilled at 85° (0.02 mm); λ_{max}^{film} 2.8, 6.12 μ.

Anal. Calcd for $C_8H_{12}O_2$: C, 68.57; H, 8.57. Found: C, 68.07; H, 8.47.

Tosylation of **4** as described for the preparation of **3a** yielded an oily tosylate, which was recovered unchanged after refluxing 18 hr in 80% acetone–water containing 4 mole equiv of potassium acetate. Treatment of this derivative with potassium *t*-butoxide as described for the preparation of **5** proceeded exothermically to give this diene.

Registry No.—**2**, 19639-98-6; **3**, 19639-92-0; **3a**, 19639-99-7; **4**, 19642-96-7; **5**, 19642-97-8; **6**, 19642-98-9.

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[3] E. M. Kosower and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 4347 (1956).

[4] E. L. Eliel and C. Pillar, *ibid.*, **77**, 3600 (1955); see also D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 1779 (1958), and references cited therein.

Reactions of Hydroxymethylferrocene. II. Sulfides[1]

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Alkyl ferrocenylmethyl sulfides have been prepared by reduction of alkyl ferrocenethiolcarboxylates with lithium aluminum hydride in the presence of aluminum chloride.[3] Nesmeyanov has reported the preparation of these compounds from ferrocenylmethanethiol,[4] and by decomposition of ferrocenylmethyltrimethylammonium iodide in the presence of aqueous sodium sulfide.[5]

We wish to report a new preparation of alkyl ferrocenylmethyl sulfides directly from hydroxymethylferro-

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[2] To whom inquiries should be addressed.

[3] D. E. Bublitz, *J. Organometal. Chem.*, **6**, 436 (1966).

[4] A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva, and Y. A. Ustynyuk, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1696 (1965); *Chem. Abstr.*, **63**, 18146 (1965).

[5] A. N. Nesmeyanov, E. G. Perevalova, L. S. Shilovtseva, and V. D. Tyurin, *Izv. Akaa. Nauk SSSR, Otd. Khim. Nauk*, 1997 (1962); *Chem. Abstr.*, **58**, 9132 (1963).