Experimental Section

All samples were run on a Varian A-60 spectrometer equipped with a variable-temperature probe. All carbamates were prepared in the same manner, and a typical preparation is given: *p*-Methoxyphenol (12.4 g) (0.1 m) was dissolved with 10.7 g (0.1 m) of dimethylcarbamoyl chloride in 30 ml of anhydrous pyridine. The solution was placed in a pressure-capped glass bottle. The bottle was heated for about 3 hr in a steam bath. The mixture was poured over ice and extracted with ether; the ether solution was washed with 10% HCl, then with $NaHCO_3$ solution, and dried for 1 hr with Na_2SO_4. Evaporation gave 12.5 g of crystalline material. Recrystallization from diethyl ether yielded *p*-methoxyphenyl N,N-dimethylcarbamate (**6**), mp 65–66° (lit.[7] mp 64–66°). In the case of *p*-fluorophenyl N,N-dimethylcarbamate (**5**), however, instead of aqueous $NaHCO_3$, 10% aqueous NaOH was necessary to wash the ethereal solution free of the phenol. After the solution was dried and evaporated with a flash evaporator, a gas chromatogram of the product showed only a trace of ether and no phenol, which would have appeared if present.

Anal. Calcd for $C_9H_{10}FNO_2$: C, 58.96; H, 5.50; N, 7.65. Found: C, 58.77; H, 5.61; N, 7.78.

p-Nitrophenyl N,N-dimethylcarbamate (**7**) was obtained in nearly 100% yield, mp 103° (lit.[8] mp 107–109°). Compounds **1**, **2**, **4**, **11**, and **12** were gas chromatographically pure. However, **12** was found to contain two products by tlc.[9]

Registry No.—**1**, 7541-16-4; **2**, 7541-17-5; **3**, 3553-80-8; **4**, 7541-19-7; **5**, 7541-20-0; **6**, 7305-10-4; **7**, 7244-70-4; **8**, 6969-90-0; **9**, 7305-08-0, **11**, 2532-49-2; **12**, 119-38-0.

Acknowledgments.—The authors are grateful to Ernest G. Pappas and Edward P. Ragelis of the Food and Drug Administration for the synthesis of some of the compounds appearing in Table I, to H. Moorefield of Union Carbide Corp., for supplying us with compound **10**, to Dr. T. M. Valega, U. S. Department of Agriculture, for allowing us to see, prior to publication, his manuscript on nmr studies of some N,N-dimethylcarbamates, and to T. E. Norris for some initial technical assistance.

(8) L. W. Dittert and T. Higuchi, *J. Pharm. Soc.*, **52**, 852 (1963).

(9) J. M. Finocchiaro and W. R. Benson, *J. Assoc. Offic. Anal. Chemists*, in press.

Homolytic Aromatic Substitution. VII. Phenylation of [2.2]Paracyclophane[1]

S. CARLTON DICKERMAN AND NORMAN MILSTEIN

Department of Chemistry, New York University, University Heights, New York, New York 10453

Received July 28, 1966

During an extensive investigation of the chemistry of paracyclophanes Cram and co-workers observed that [2.2]paracylophane is considerably more reactive in acetylation than any of the larger members of the series.[2] Furthermore, the monoacetyl derivative of [2.2]paracyclophane is strongly deactivated toward further substitution in both rings.[3] These effects have been attributed to transannular delocalization in both types of cations, that is, to $\sigma-\pi$ overlap.[2] Since any rate enhancement in electrophilic aromatic substitution usually has a counterpart in homolytic aromatic substitution, the phenylation of [2.2]paracyclophane was studied to determine whether rate enhancement is observable in the latter type of reaction.

The required 4-phenyl[2.2]paracyclophane was prepared conveniently by direct phenylation of the parent hydrocarbon in pyridine with N-nitrosoacetanilide. Ring substitution was established by nmr spectroscopy and by comparison of retention times in glpc of a sample prepared, but not isolated in sufficient amounts to permit characterization, by treatment of 4-amino-[2.2]paracyclophane[3] with isoamyl nitrite in benzene.[4]

Quantitative measurements of reactivity were determined in the solvent pyridine–benzene using N-nitrosoacetanilide as the source of phenyl radicals.[5] We had hoped to compare N-nitrosoacetanilide and Meerwein phenylations of [2.2]paracyclophane but the insolubility of this arene in the usual solvent system, acetone–water, prevented use of the latter method of arylation. The pertinent data, determined by glpc, are given in Table I and reveal that the molecular reactivity of [2.2]paracyclophane is 33 times as great as that of benzene. In view of the fact that homolytic phenylation is one of the least selective substitution reactions known, a total rate factor of 33 is surprising. For example, both naphthalene[6] with eight and phenanthrene[7] with ten reaction sites, respectively, exhibit a total rate factor of only 16.

TABLE I

N-NITROSOACETANILIDE PHENYLATION OF [2.2]PARACYCLOPHANE

Run[a]	Biphenyl,[b] mmoles	4-Phenyl[2.2],[b] mmoles	TRF[c]	Yield, %	Recovery,[d] %
1	0.0154 ± 0.0008	0.00531 ± 0.0026	32.5 ± 2.8	4.4 ± 0.2	92 ± 1
2	0.0168 ± 0.0003	0.00594 ± 0.0009	33.2 ± 1.0	5.0 ± 0.1	89 ± 3

[a] The data for each run represent an average of three determinations. [b] Based on 0.120 mmole of [2.2]paracyclophane and 11.2 mmoles of benzene; see the Experimental Section for details. [c] Total rate factor. [d] Recovery of [2.2]paracyclophane including 4-phenyl[2.2]paracyclophane.

A total rate factor of 33 in the phenylation of [2.2]-paracyclophane is equivalent to a partial rate factor of 25; *i.e.*, each position in [2.2]paracyclophane is 25 times as reactive as a position in benzene. However, it can be argued that the usual concept of partial rate factor is not strictly applicable in assessing the reactivity of [2.2]paracyclophane. For example, there is compelling evidence that the transition state for radical addition to arenes is one in which the attacking radical is oriented essentially perpendicular to, rather than in, the nodal plane.[6,8,9] If the phenylation of [2.2]paracyclophane is mechanistically analogous, each position in this hydrocarbon is exposed to reaction at only one face of the nodal plane while each site in ordinary arenes is doubly exposed. Therefore, in homolytic phenylation the reactivity at each position in [2.2]paracyclophane

(1) Supported in part by an Institutional Grant (1N-146) from the American Cancer Society.

(2) D. J. Cram, W. J. Wechter, and P. W. Kierstead, *J. Am. Chem. Soc.*, **80**, 3126 (1958).

(3) D. J. Cram and N. L. Allinger, *ibid.*, **77**, 6289 (1955).

(4) J. I. G. Cadogan, *J. Chem. Soc.*, 4257 (1962).

(5) The mechanism of the decomposition of N-nitrosoacetanilide has been established recently by C. Rüchardt and B. Freudenberg, *Tetrahedron Letters*, No. 48, 3623 (1964).

(6) S. C. Dickerman and G. B. Vermont, *J. Am. Chem. Soc.*, **84**, 4150 (1962).

(7) S. C. Dickerman and I. Zimmerman, unpublished results.

(8) J. H. Binks, J. Gresser, and M. Szwarc, *J. Chem. Soc.*, 3944 (1960).

(9) H. Weingarten, *J. Org. Chem.*, **26**, 730 (1961).

is in effect about 50 times that of any position in benzene.

A part of the reactivity of [2.2]paracyclophane may be attributed to the presence of the four methylene groups. *p*-Xylene was selected as a model compound for estimating the magnitude of this effect[10] and the reactivity of this arene, relative to benzene, was measured under the same reaction conditions employed for the phenylation of [2.2]paracyclophane. The total rate factor of *p*-xylene was found to be 2.4, in good agreement with the value of 2.7 reported by Huisgen and Sorge[11] before the advent of glpc. Therefore, the total and partial rate factors for homolytic phenylation of [2.2]paracyclophane, relative to *p*-xylene, are 14 and 7, respectively. If the argument advanced in the preceding paragraph is accepted, the sterically corrected reactivity at each position in [2.2]paracyclophane is 14 times as great as that of any site in *p*-xylene. Such rate enhancement could arise from transannular stabilization of and/or relief of strain in the transition state leading to the intermediate or cyclohexadienyl type of radical. An examination of molecular models of this radical reveals that strain may be relieved if the radical adopts a nonplanar conformation. However, any effect of this kind must be largely counterbalanced by a loss in delocalization energy in the ring undergoing substitution. The alternative interpretation is transannular delocalization through σ–π overlap in the planar radical. Since substantial amounts of this type of bonding could be maintained in a nonplanar radical, it is not inconceivable that both effects, relief of strain and transannular delocalization, contribute to rate enhancement in homolytic, and possibly electrophilic, aromatic substitution of [2.2]paracyclophane.[12]

Experimental Section[13]

4-Phenyl[2.2]paracyclophane.—Solid N-nitrosoacetanilide (12 g) was added to a solution of 1.08 g of [2.2]paracyclophane in 50 ml of pyridine at 65° under nitrogen and with stirring. After reaction, the pyridine was removed under vacuum and the residue was dissolved in 50 ml of methylene chloride. This solution was extracted with dilute hydrochloric acid, washed with water, dried, concentrated, and placed on an alumina column (Woelm, neutral, activity grade 1). Elution with cyclohexane gave an oil which was crystallized from methanol–cyclohexane–absolute ethanol. Recrystallization from absolute ethanol gave 76 mg of 4-phenyl[2.2]paracyclopame: mp 114–116°; λ_{max}^{EtOH} 222 mμ (log ϵ 4.47); nmr (CCl_4, internal TMS) τ 2.57 (five aromatic protons), 3.48 (seven aromatic protons), and a complex multiplet centered at 6.9 (eight methylene protons).

Anal. Calcd for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.87; H, 7.05.

Treatment of 4-amino[2.2]paracyclopane[3] with isoamyl nitrite in benzene[4] gave impure material in low yield. However, the major component of this mixture exhibited the same retention time (glpc) as the sample prepared as described above.

Phenylation of [2.2]Paracyclophane.—N-nitrosoacetanilide (100 mg), 25 mg (0.120 mmole) of [2.2]paracyclophane, and 1.00 ml (11.2 mmoles) of benzene were dissolved in 5 ml of pyridine in a 6-in., side-arm test tube under nitrogen. After standing at 25–30° overnight, the mixture was dissolved in 35 ml of methylene chloride. This solution was extracted with two portions of dilute hydrochloric acid, washed with water, and dried, and the solvent was removed under reduced pressure. The residue was dissolved in the minimum amount of benzene, and *p*-chlorobiphenyl and pyrene were added as internal standards. Analyses were accomplished with a pair of 6 ft × 1/8 in. columns packed with 10% SE-30 on 80–100 mesh Chromosorb P. Total rate factors and recoveries were measured by programming from 125 to 250° at 4 and 8°/min, respectively. The results are given in Table I.

Phenylation of *p*-Xylene.—To a 6-in., side-arm test tube were added 150 μl (1.21 mmoles) of *p*-xylene, 1.00 ml (11.2 mmoles) of benzene, 5 ml of pyridine, and 100 mg of N-nitrosoacetanilide under nitrogen. After reaction, the products were isolated and analyzed as described above for the phenylation of [2.2]paracyclophane except that naphthalene was used as the internal standard. Authentic 2,5-dimethylbiphenyl was prepared from 2,5-dimethylaniline by treatment of this amine with isoamyl nitrite in benzene.[4] Duplicate runs gave a total rate factor of 2.42 ± 0.04 (lit.[11] 2.7). None of the products of this reaction exhibited a retention time corresponding to that of authentic 4,4′-dimethylbibenzyl.

Registry No.—[2.2]Paracyclophane, 1633-22-3; 4-phenyl[2.2]paracyclophane, 7603-30-7; biphenyl, 92-52-4.

(10) No model is entirely satisfactory. For example, 1,4-diethylbenzene was considered and rejected because previous studies of the phenylation of ethylbenzene have revealed some steric hindrance to reaction at the *ortho* positions in this arene: G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press Inc., New York, N. Y., 1960, p 76.

(11) R. Huisgen and G. Sorge, *Ann.*, **566**, 162 (1950).

(12) See ref 2 for an assessment of strain in the cation and the conclusion that formation of this species may lead to an increase in strain.

(13) Melting points are corrected. Ultraviolet and nmr spectra were observed on Cary Model 14 and Varian A-60 spectrophotometers, respectively. An F & M Model 810 gas chromatograph with dual hydrogen-flame detectors and a Disc integrator were employed to determine the reactivity data. Elemental analyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

Reaction of Diphenylphosphinyl Azide with Diphenylphosphine

REINHOLD H. KRATZER AND KAY L. PACIOREK[1a]

MHD Research, Inc., Newport Beach, California 92663

Received September 16, 1966

The phosphonitrilic derivatives of the general formula $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_nOH$, where $n = 1$ and 3, are easily accessible by the hydrolysis of $[(C_6H_5)_2P(NH_2)NP(C_6H_5)_2(NH_2)]Cl$[1b] and $(C_6H_5)_2P(O)[N{=}PC_6H_5)_2]_3Cl$[2], respectively. The compound with $n = 2$ to date was obtained only as a reaction by-product in very poor yield.[2] The peculiar interaction of triphenylsilyl azide with diphenylphosphine[3] should be adaptable to the preparation of $(C_6H_5)_2P(O)[N{=}P(C_6H_5)_2]_2OH$, providing the rearrangement step of this reaction is a general one and independent of the type of azido compound subjected to reaction with a secondary phosphine.

Thus equimolar amounts of diphenylphosphinyl azide and diphenylphosphine were mixed in benzene solution at room temperature. Nitrogen evolution was observed after an incubation period of about 5 min, whereas the reaction between triphenylsilyl azide and diphenylphosphine required heating to 138°.[3] The desired product (II) was obtained in a 64% yield [based on $(C_6H_5)_2P(O)N_3$ employed], together with a small quantity of what is believed to be the intermediate I of the following reaction sequence. In

(1) (a) The Marquardt Corp., Newport Beach, Calif. 92663; (b) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

(2) K. L. Paciorek, *ibid.*, **3**, 96 (1964).

(3) K. L. Paciorek and R. H. Kratzer, *J. Org. Chem.*, **31**, 2426 (1966).