Distillation of the product gave 0.66-g. forerun, b.p. 42–50° (6 mm.), identical in infrared spectrum with benzylamine, and 4.05 g. (67%) of 5-benzylamino-1-pentanol, b.p. 152–168° (6 mm.), lit.[4] b.p. 174–178° (11 mm.). The infrared spectrum was compatible with the assigned structure.

5-Piperidino-1-pentanol from Pentamethylene Chlorohydrin.—In a 250-ml. three-necked flask equipped with a condenser, magnetic stirrer, dropping funnel, and thermometer were placed 25.5 g. (0.3 mole) of piperidine and a pellet of potassium hydroxide in 100 ml. of water. Pentamethylene chlorohydrin (13.9 g., 0.1 mole) was added dropwise at room temperature. The mixture was then heated at about 78° for 2 hr. and cooled. Potassium hydroxide pellets were added until two layers formed. These were separated, and the aqueous layer was extracted with three 100-ml. portions of diethyl ether. The ether extracts were combined with the original organic material, dried over potassium carbonate, and concentrated. Distillation at 175 mm. led to removal of excess piperidine. The residue distilled at 100–112° (5.5 mm.), $n^{18}\mathrm{D}$ 1.4799, and weighed 12.7 g. (74%); lit.[7] b.p. 140° (13 mm.), $n^{15.5}\mathrm{D}$ 1.4820.

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The Gomberg–Bachmann Reaction with Benzene-*d*

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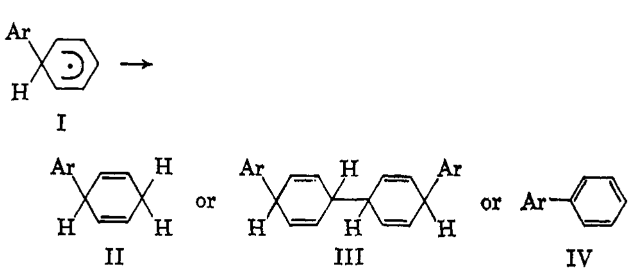
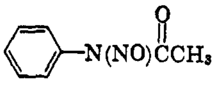
Previous work[2,3] has shown that free-radical arylation[4] of benzene with diaroyl peroxides involves arylcyclohexadienyl radicals (I) as intermediates. Among the criteria employed to demonstrate the intermediacy of these radicals has been isolation of their disproportionation and dimerization products[2] [dihydrobiaryls (II) and tetrahydroquateraryls (III)], an apparent isotope effect in the formation of arylbenzene (IV) when benzene-*d* is the substrate,[3] and the appearance of dideuterated biaryls with the same starting material.[3] The apparent isotope effect is due to a discrimination between 1-deuterated 1-arylcyclohexadienyl radicals and undeuterated arylcyclohexadienyl radicals in regard to hydrogen abstraction (to give IV) *vs.* hydrogen acceptance or dimerization (to give II or III). Dideuterated biaryls result from dehydrogenation[5] of dideuterated dihydrobiaryls which arise in the disproportionation process when the substrate is benzene-*d*.



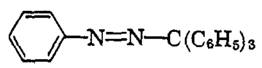
I

II III IV

The failure of the above three criteria in the case of arylation with nitrosoacetanilide (NAA) and phenylazotriphenylmethane (PAT)[6] was originally interpreted



NAA



PAT

to indicate that free arylcyclohexadienyl radicals (I) are not intermediates in arylation with these reagents. Instead, the intervention of certain caged radicals was postulated.[6] Subsequently, however, it was pointed out[7-9] that the absence of disproportionation or dimerization products does not rule out the intervention of arylcyclohexadienyl radicals. Rather, this failure may be ascribed to the presence, in relatively high stationary-state concentrations, of radicals that can act as efficient hydrogen abstractors. With such radicals present, the arylcyclohexadienyl radicals (I) give hydrogen to yield IV before they have an opportunity to disproportionate or dimerize to give II or III. In the case of PAT,[7,8] the relatively stable hydrogen abstractor is the triphenylmethyl radical $Ph_3C\cdot$. With benzoyl peroxide as the radical source, there is no corresponding stable hydrogen abstractor (benzoate radicals being rather fleeting), and so dimerization and disproportionation become important side reactions to arylation.

It was less clear why there is little or no disproportionation or dimerization when the arylating reagent is NAA. Clearly, assuming a high stationary state concentration of acetate radicals as hydrogen abstractors is unreasonable in view of the known[10] instability of these radicals. Nevertheless, "cage effects" are not involved.[11]

The long-standing mystery of the NAA reaction has now been elegantly solved by Rüchardt and coworkers,[12,13] who have presented convincing evidence[13] that NAA is converted to a diazoanhydride, ArN=N—O—N=NAr, prior to arylation. The diazoanhydride then gives rise to Ar· (the arylating agent), nitrogen, and Ar—N=N—O·. The latter radical is rather stable and thus, like $Ph_3C\cdot$, accumulates in quite high stationary-state concentration and acts as an efficient scavenger for the arylcyclohexadienyl radicals I, preventing their dimerization and disproportionation and converting them, instead, to arylbenzene IV and ArN=N—OH. The latter then reacts

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[1] The Radiation Laboratory is operated under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-413.

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[9] See also G. A. Russell and R. F. Bridger, *ibid.*, 737 (1963).

[10] *E.g.*, L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957); M. J. Goldstein, *Tetrahedron Letters*, 1601 (1964).

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[13] C. Rüchardt and B. Freudenberg, *ibid.*, 3623 (1964).

with NAA (or rather its rearrangement product,[14] the diazonium acetate) to give acetic acid and regenerate ArN=N—O—N=NAr.

Rüchardt has also investigated[12] the Gomberg–Bachmann reaction,[15] in which the arylating reagent is a diazonium salt and base, and has shown that in this case, also, the diazoanhydride is an essential intermediate. Here again the arylcyclohexadienyl radicals are scavenged (to give arylbenzenes) efficiently by ArN=NO· radicals.

In view of the similarity of the Gomberg–Bachmann and NAA reactions established by Rüchardt, it was to be expected that the former would also lack the criteria of dihydrobiaryl formation, apparent isotope effects, and appearance of dideuterated biaryls. As it happens, we had already obtained the pertinent data for the Gomberg–Bachmann reaction of benzene-*d* with *p*-methyl-, *p*-methoxy-, and *p*-chlorobenzenediazonium salts and are placing them on record at this time to round out the now well-understood picture of free-radical arylation. Table I gives the calculated apparent isotope effects and per cent of dideuterated biaryl in the Gomberg–Bachmann arylations indicated (each carried out in duplicate). The isotopic purity of starting benzene-*d* and the deuterium content of biaryl, both determined mass spectrometrically, are also included.

TABLE I

GOMBERG–BACHMANN REACTIONS WITH BENZENE-*d*

Arylating group	Apparent isotope effect[a]	Mole % biaryl-d_2[b]	Isotopic purity of benzene-*d*, mole %	Mole % biaryl-d_1
p-$CH_3C_6H_4$	1.01	0.10	97.02	80.85
p-$CH_3C_6H_4$	0.99	0.13	97.02	80.54
p-$CH_3OC_6H_4$	1.03	0.08	97.12	81.25
p-$CH_3OC_6H_4$	1.00	0.11	97.12	80.65
p-ClC_6H_4	1.07	0.04	97.18	81.73
p-ClC_6H_4	1.07	0.08	97.18	81.72

[a] Apparent isotope effects up to 1.12 were obtained in the NAA and PAT reactions previously. In contrast, apparent isotope effects in the diaroyl peroxide reactions usually range from 1.3 up. [b] Comparable data for NAA and PAT reactions are 0.0–0.23 mole %, for diaroyl peroxide reactions 0.39–0.53 mole %.

Our results suggest the presence of an efficient radical scavenger in the intermediate stages of the Gomberg–Bachmann reaction, and are in complete agreement with Rüchardt's postulated mechanism.

Experimental

Gomberg–Bachmann Reaction.—The reaction of *p*-toluidine is typical. *p*-Toluidine (0.58 g., 5.4 mmoles) was dissolved in 2 ml. of concentrated hydrochloric acid and diazotized at 0–5° with 0.6 g. of sodium nitrite dissolved in 2 ml. of water. The solution of the resulting diazonium salt was added slowly, with vigorous stirring, to a mixture of 30 g. (0.38 mole) of benzene-*d* (97.02% isotopically pure by mass spectrometry at reduced ionizing voltage) and aqueous sodium acetate (3.0 g. in 7 ml. of water) maintained at 6–10°. After completion of the addition, the mixture was stirred at 6–10° for 0.5 hr. and then at room temperature for 6 hr. The dark benzene layer was separated, washed three times with aqueous sodium bicarbonate followed by water, dried over calcium chloride, and concentrated on a steam bath. The residue was dissolved in 5 ml. of ether, mixed with 2 g. of activated alumina, and dried in a film evaporator. The residue, impregnated on alumina, was placed on top of an alumina column (25 g.) and was extracted repeatedly with petroleum ether (b.p. 60–90°). The first 100 ml. of eluate on concentration gave *ca.* 350 mg. of 4-methylbiphenyl, m.p. 42–44.5°, raised to 46.5–47° (lit.[3] m.p. 46.5–48°) by sublimation under reduced pressure and crystallization from methanol.

Anal.[16] Calcd. for $C_{13}H_{11.19}D_{0.81}$: C, 92.36; H, 7.15; D, 6.77 atom %. Found: C, 92.01, 92.05; H, 7.10, 7.22; D, 6.60 atom %.

Anal.[16] Calcd. (for the second experiment): D, 6.71 atom %. Found: C, 92.40; H, 7.16; D, 6.56 atom %.

p-Methoxybiphenyl was prepared similarly and had m.p. 89.5–90° (lit.[3] m.p. 89°).

Anal.[16] Calcd. for $C_{13}H_{11.19}D_{0.81}$: C, 84.38; H, 6.54; D, 6.77 atom %. Found: C, 84.12; H, 6.52; D, 6.78 atom %.

Anal.[16] Calcd. (for the second experiment): D, 6.72 atom %. Found: C, 84.23; H, 6.44; D, 6.74 atom %.

p-Chlorobiphenyl was prepared analogously and had m.p. 79–79.5° (lit.[3] m.p. 78.5–79°).

Anal.[16] Calcd. for $C_{12}H_{8.18}D_{0.82}$: C, 76.10; H, 4.79; D, 9.08 atom %. Found: C, 76.25, 76.35; H, 4.85, 4.76; D, 9.07, 9.05 atom %.

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[16] Analyses are based on the assumption of H–D exchange in the analyst's train (*cf.* ref. 3) and were performed by Mr. Josef Nemeth, Urbana, Ill.

Structure of Salts of 4,6-Dinitrobenzofuroxan[1]

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The structure of salts of 4,6-dinitrobenzofuroxan (I) became of interest because elemental analysis indicated that the salts are hydrated, but the investigators could not conclusively determine the amount of water present.[3–7] A cursory study questioned the concept of water of hydration because the water in the potassium salt was not evolved at temperatures up to the decomposition temperature of 160° and because of the sharpness of the O–H stretching mode at 3480 cm.$^{-1}$, shown by infrared spectroscopy.

Drost[3] suggested loss of a ring proton to give an anion such as II and simple hydration of the salt. Gaughran,[7] *et al.*, proposed the same structure owing to the similarity of the infrared spectrum of I and the various salts.

Various structures chemically incorporating the equivalent elements of water as shown (III to V) were considered. However, subsequently it was found that Jackson and Earle[6] had proposed, without experimental evidence, similar structures.

Experimental facts from deuteration studies and proton magnetic resonance prove that structures II and III are not possible. Structures IV and V are

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[1] This contract was supported by Sandia Corp. through purchase order 13-7664.

[2] This is an essential portion of a thesis submitted to the Metallurgy Department, University of Utah, in a partial fulfillment of the requirement for a Doctor of Philosophy Degree.

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