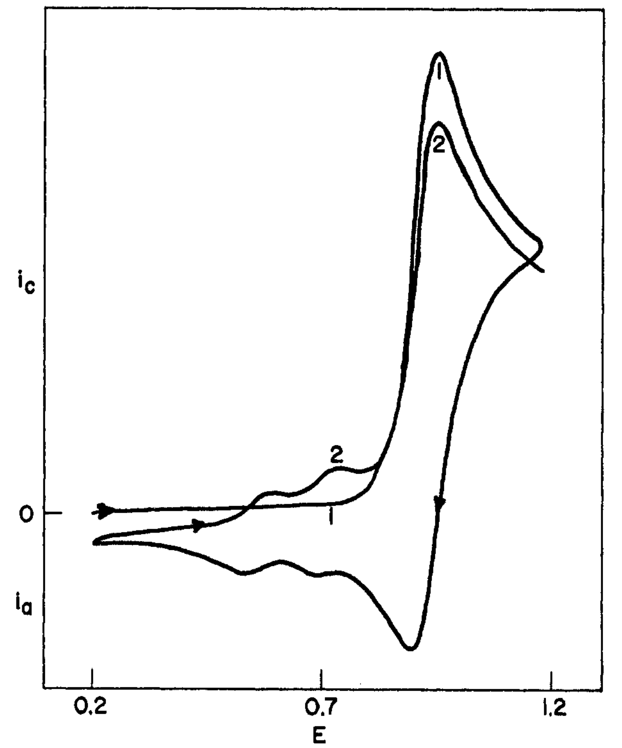

Figure 2.—Cyclic voltammogram of 5.52×10^{-3} M p-iodonitrobenzene and 0.1 M $NaNO_2$ in 0.1 M TEAP–DMSO at a scan rate of 80.6 mV/sec.

This work illustrates the facile nature of the coupling process of an organic free radical and anion. In contrast to the earlier reported work utilizing relatively stable benzyl free radicals,[2] the results reported herein illustrate that reactive phenyl radicals can be effectively scavenged by various anions even in the presence of reasonably good hydrogen-donating solvents. Such a low-energy reaction pathway available to free radicals is understandable, since only bond-formation and no bond-cleavage processes are involved.

Experimental Section

Instrumentation.—The cyclic voltammetric and thin-layer coulometric studies were performed on a transistorized, three-electrode potentiostat–galvanostat described previously.[4] The techniques suggested by Brown, Smith, and Booman[12] for stabilization of the potentiostat with 100% iR compensation were incorporated into this instrument.

Electron spin resonance spectra were obtained on a Varian V-4502 spectrometer. The anion radicals were produced *in situ* by the electrochemical reduction of the required iodonitrobenzene in the presence of the reacting anion.

The gas chromatograph was a Hewlett–Packard Model 700 equipped with flame ionization detection.

Cells and Electrodes.—The working electrode in the cyclic voltammetric experiments was a planar platinum button (Beckman No. 39273) with a geometric area of *ca.* 0.23 cm^2. The auxiliary electrode, a platinum foil, and the reference electrode, a saturated calomel electrode (sce), were isolated from the working electrode compartment by means of porous vycor glass (Corning No. 7930) and a bridge containing the solvent and 0.1 M supporting electrolyte.

A thin-layer electrode similar to the one described by McClure and Maricle[13] was used for the rapid determination of n values. The working electrode was a 3-mm length of 0.25-cm-diameter platinum rod attached to a stainless steel spindle (L. S. Starrett Co.) by means of electrically conducting epoxy. The sides of the spindle and the platinum rod were covered with a thin layer of epoxy cement (Devcon WR-2) in order to render them electroinactive. While the electrode functioned well in solutions of DMSO and AN, degradation of the epoxy covering occurred within several hours after placement in DMF solutions.

In the thin-layer experiments the potential of the working electrode was set sufficiently cathodic so as to reduce iodonitrobenzene and nitrobenzene (the product of hydrogen atom abstraction), but not so cathodic as to further reduce the product of the coupling reaction with cyanide ion. The method is not applicable in the case of nitrite ion, since the product of the coupling reaction, a dinitrobenzene anion radical, is further reduced at the applied potential to the corresponding dianion.

Chemicals.—All organic compounds were commercially available samples. The purity of each was checked by gas chromatography, cyclic voltammetry, and melting point; impure samples were recrystallized repeatedly until at least 99% purity was obtained.

Tetraethylammonium perchlorate was prepared according to the method of Kolthoff and Coetzee;[14] the method of Pocker and Kevill[15] was used for the preparation of tetraethylammonium nitrite. All supporting electrolytes were stored in a vacuum desiccator prior to their use. In a typical experiment, data were obtained first for the particular electrochemical system with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. The experiment was then repeated with the sodium salt of the desire anion added (0.1 M). Because of the insolubility of sodium nitrite in AN, tetraethylammonium nitrite was used as the anion source in this solvent.

DMF, AN, and DMSO were purified by previously described procedures[4] and stored over Linde Type 4A molecular sieves. All electrochemical experiments were performed in a glovebag under a nitrogen atmosphere. The solutions were deaerated with purified nitrogen for at least 20 min prior to the electrochemical measurements. All work was conducted at room temperature (22.5 ± 0.5°).

In the thermal generation of phenyl radicals, phenylazotriphenylmethane (0.005 M) was decomposed at 60.0 ± 0.1° with DMSO containing 0.10 M $NaNO_2$. Gas phase chromatography analysis showed formation of both benzene and nitrobenzene.

Registry No.—**1**, 636-98-6; **3**, 2395-99-5; p-nitrobenzonitrile anion radical, 12402-47-0; 3-iodonitrobenzene, 645-00-1; m-nitrophenyl radical, 3522-58-5; m-nitrobenzonitrile anion radical, 12402-46-9; 2-iodonitrobenzene, 609-73-4; o-nitrophenyl radical, 23209-57-6; o-nitrobenzonitrile anion radical, 12402-45-8.

Acknowledgments.—Acknowledgment is made to the Kansas State Bureau of General Research for partial support of this work and to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant PRF 1123-G1).

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[12] E. R. Brown, D. E. Smith, and G. L. Booman, *Anal. Chem.*, **40**, 1411 (1968).

[13] J. E. McClure and D. L. Maricle, *ibid.*, **39**, 236 (1967).

[14] I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 870 (1957).

[15] Y. Pocker and D. N. Kevill, *ibid.*, **87**, 4760 (1965).

The Reaction of Benzyne with 1,3-Cyclohexadiene

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The recent report by Grisdale, *et al.*,[2] describing the synthesis and characterization of the series of phenyl-

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[1] J. R. Geigy A. G., 1061.419 Grundlagenforschung, 4000, Basel 21, Switzerland.

[2] P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. R. Williams, *J. Org. Chem.*, **33**, 1116 (1968).

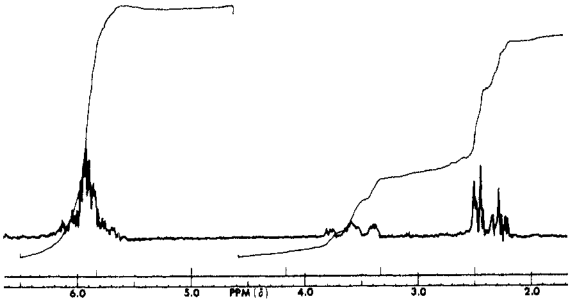


Figure 1.—Nmr spectrum of 5-phenyl-1,3-cyclohexadiene (**3**).

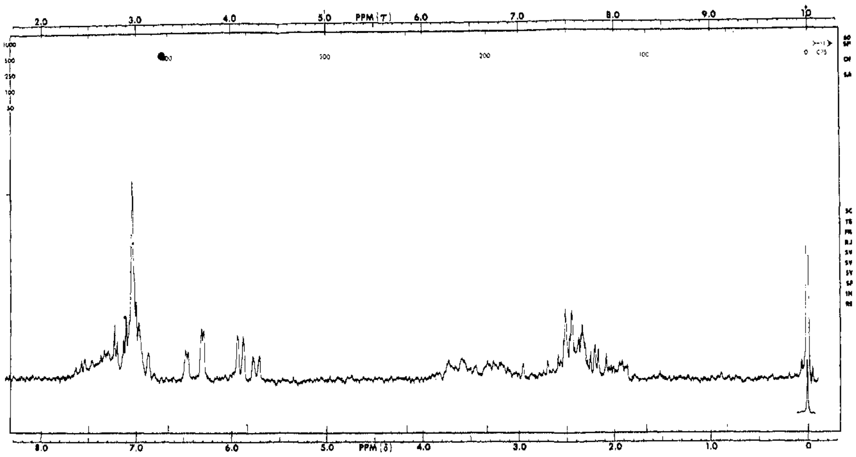


Figure 2.—Nmr spectrum of 4,5-benzobicyclo[4.2.0]octa-2,4-diene (**5**).

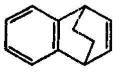
cyclohexadienes prompts us to report information concerning the reaction of benzyne with 1,3-cyclohexadiene.

This reaction has been reported by Simmons[3a] and further investigated by Huisgen and Knorr.[3b] The principal product, 5,6-benzobicyclo[2.2.2]octa-2,5-diene (**1**), has been identified by ir and nmr spectroscopy. In addition, Simmons isolated a mixture of isomers and suggested that the nmr spectrum of the mixture is consistent with the presence of a benzocyclobutene ring system.[3a]

Besides **1**, Huisgen and Knorr isolated three other products and tentatively assigned structures **2** and **3** for two of them.

Via Simmons' procedure and preparative vapor chromatography using a 39 ft × 0.75 in. o.d. stainless steel column, packed with 25% Carbowax 20M on 30–60 Chromosorb W, with a column temperature of 150° and an injector temperature of 180°, triphenylene, **1**, **2**, **3**, and another isomer were isolated. The structural assignments were based upon nmr and uv spectroscopy of the analytical pure products.

5,6-Benzobicyclo[2.2.2]octa-2,5-diene (**1**) was identified by comparing the nmr data with those published by Tori, *et al.*[4,5] 3-Phenyl-1,4-cyclohexadiene (**2**), has been adequately characterized by Grisdale, *et al.*[2] The integration of the nmr spectra of both **2** and **3** gave identical group integral ratios: five aromatic, four olefinic, one benzylic, and two allylic protons. As would be expected of an asymmetric structure, the signals for the olefinic protons of **3** are very complicated multiplets. Signals for the benzylic and allylic protons of **3** appeared at appreciably higher field, δ 3.60 and 2.38, respectively, than those of **2** (*cf.* Figure 1 and ref 2). This is consistent with the assigned structures, since the protons in question are monoallylic in **3** and bisallylic in **2**. The uv spectrum of **3** showed a broad absorption at 259 nm (ε 5100) in contrast to the absorption bands of **2**, which were found similar to those reported by Grisdale, *et al.*[2]



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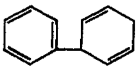

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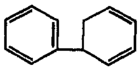

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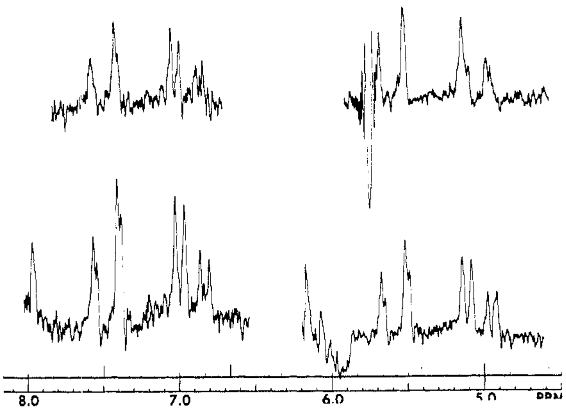

Figure 3.—Double-resonance experiments with 4,5-benzobicyclo[4.2.0]octa-2,4-diene: left, no decoupling by irradiating at δ 3.6; right, decoupling by irradiating at δ 3.2.

Because most of the benzyne reactions with dienes are known to yield 1,2 as well as 1,4 addition, we considered structure **4** for the fifth product, which appeared in a yield of 3%. However, the ultraviolet spectrum shows a maximum at 248 nm (ε 8600),[6] typical of styrene derivatives.[7] The nmr spectrum (Figure 2) shows four aromatic and two olefinic protons and two and four protons at δ 3.2. and 2.4, respectively. In double-resonance measurements, the frequencies as-

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[3] (a) H. E. Simmons, *J. Amer. Chem. Soc.*, **83**, 1657 (1961); (b) R. Huisgen and R. Knorr, *Tetrahedron Lett.*, 1017 (1963).

[4] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

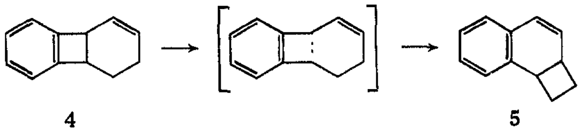
[5] K. Tori, Y. Hata, R. Muneyuki, Y. Takano, T. Tsuji, and H Tanida, *Can. J. Chem.*, **42**, 926 (1964).

[6] This compound is very sensitive to air; the ε value might be too low.

[7] R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1951.

signed to olefinic protons (δ 6.35 and 5.84) were saturated without noticeable effect on the methylene signals. However, decoupling by saturation of the frequency of one of the bridgehead protons (δ 3.2, *cf.* Figures 2 and 3) led to simplification of the signals in the olefinic region. The combined results point strongly to **5** as the structure of the new product.

We speculate that 4,5-benzobicyclo[4.2.0]octa-2,4-diene (**5**) is produced by thermal rearrangement from **4**, which may be unstable under the conditions of vapor chromatographic work-up.



4 5

Registry No.—**3**, 21473-05-2; **5**, 21367-71-5; benzyne, 462-80-6; 1,3-cyclohexadiene, 592-57-4.

Acknowledgment.—This work was supported by a grant from the National Science Foundation. I am grateful to Professor George S. Hammond for his sponsorship of the work and for helpful discussion of the results, and to Dr. Christian Tanzer for his help in the double-resonance experiments.

A New Electrochemical Method for the Selective Reduction of Aliphatic Amides to Aldehydes or Alcohols

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Although the reduction of aliphatic amides to alcohols and aldehydes has been reported, the reaction has been limited to rather specific compounds. Thus aldehydes were obtained from amides using sodium in liquid ammonia,[1] but reaction occurred only with compounds possessing a phenyl group attached either to the nitrogen atom or to the carbonyl carbon.

The reduction of amides has also been accomplished electrolytically, but, here again, the substrates were quite specific, *e.g.*, N-aryl amides,[2] amides of isonicotinic acid,[3] and 2-carboxythiazole.[4] It was our purpose to develop a general and selective method, if possible, for the electrolytic reduction of primary, secondary, and tertiary amides to either the corresponding alcohol or aldehyde.

The reductions were carried out in an undivided electrolytic cell[5] consisting simply of a three-neck, round-bottom flask fitted with a Dry Ice condenser and two platinum electrodes. Lithium chloride dissolved in monomethylamine was used as electrolyte.

As can be seen (Table I), alcohols were obtained as major product when the reductions were carried out in the absence of an added proton source like ethanol. Further, it can be seen that the yield of alcohol product was generally good and not adversely affected by the length of the carbon chain of the starting amide or by substitution of one or two alkyl groups on the amide nitrogen.

TABLE I[a]

ELECTROREDUCTION OF VARIOUS ALIPHATIC AMIDES TO THE CORRESPONDING ALDEHYDE OR ALCOHOL

Entry	Amide[b]	Alcohol, %	Aldehyde, %	Coulombs
1	$CH_3(CH_2)_4CONH_2$ (0.05, 700)	58[c]	...	50,400
2	$CH_3(CH_2)_6CONH_2$ (0.01, 350)[d]	...	22	14,400
3	$CH_3(CH_2)_8CONH_2$ (0.05, 700)	59[c]	...	50,400
4	$CH_3(CH_2)_8CONH_2$ (0.005, 350)[e]	...	28	14,400
5	$CH_3(CH_2)_{12}CONH_2$ (0.02, 450)	92	...	50,400
6	$CH_3(CH_2)_{14}CONH_2$ (0.01, 450)	86	...	50,400
7	$CH_3(CH_2)_{16}CONH_2$ (0.01, 450)	79	...	50,400
8	$CH_3(CH_2)_4CONHCH_3$ (0.05, 600)[e]	4	50	12,960
9	$CH_3(CH_2)_4CONHCH_3$ (0.05, 600)	51	...	50,400
10	$CH_3(CH_2)_8CONHCH_3$ (0.02, 300)	81	...	46,800
11	$CH_3(CH_2)_8CONHCH_3$ (0.01, 300)[e]	24	58	14,400
12	$CH_3(CH_2)_8CON(CH_3)_2$ (0.008, 350)	93	...	14,400
13	$CH_3(CH_2)_8CON(CH_3)_2$ (0.01, 350)[e]	...	45	14,400
14	$CH_3(CH_2)_{14}CON(CH_3)_2$ (0.02, 450)	97	...	50,400
15	$CH_3(CH_2)_8CONH_2$ (0.005, 350)[e]	50	4	57,600

[a] The products reported in this table were identified by a combination of physical (ir and nmr spectra) and chemical methods (*e.g.*, melting points of compounds and derivatives such as 2,4-dinitrophenylhydrazones of aldehydes and 3,5-dinitrobenzoates of alcohols. [b] The first value in parentheses represents the number of moles of amide used; the second value represents the number of milliliters of methylamine employed as solvent. [c] A minor product observed in this case was the N-methylimine of the corresponding aldehyde. [d] Seven grams of ethanol present during reduction. [e] Five grams of ethanol present during reduction.

Reduction to aldehydes was achieved in the same cell and under the same reaction conditions as were used to produce alcohols, except that absolute ethanol was added to serve as a proton source. The yield of aldehydes (Table I) was not affected by the length of the carbon chain of the starting amide, but was influenced by alkyl substitution on the amide nitrogen. Reduction of secondary and tertiary amides resulted in better yields of aldehydes than reduction of primary amides.

The mechanistic scheme shown in Scheme I has been proposed[1] to explain such reaction products.

When electrolysis is conducted in the absence of ethanol, the equilibrium between I and II (path b)

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[1] A. J. Birch, J. C. Craig, and M. Slaytor, *Aust. J. Chem.*, **8**, 512 (1955).

[2] L. Horner and H. Neuman, *Chem. Ber.*, **98**, 3462 (1965).

[3] H. Lund, *Acta Chem. Scand.*, **17**, 2325 (1963).

[4] P. Iversen and H. Lund, *ibid.*, **21**, 389 (1967).

[5] R. A. Benkeser and E. M. Kaiser, *J. Amer. Chem. Soc.*, **85**, 2858 (1963).