in ethanol effects complete conversion in 30 min, acid alumina causes rapid isomerization, etc. Both analyses and spectra confirm the assigned structure. This reaction finds analogy in the highly facile acid-induced ring opening of the spiropentene **2** to the triafulvene **9**.[6]

The nature of the intermediate(s) that leads to heptafulvalene and spirononatriene is, of course, questionable.[11] However, whatever its structure, the products that it gives rise to are those anticipated for a carbene (dimer formation) of low electrophilicity (no reaction with alkenes) and relatively high nucleophilicity (reaction with electrophilic double bonds).

Acknowledgment. The authors gratefully acknowledge the support of this research by the U. S. Army Research Office, Durham.

(11) Reaction of heptafulvalene with dimethyl fumarate in a reaction analogous to that proposed by Lemal[3] to explain the products of reaction of electrophiles with tetraaminoethylenes was independently excluded as the source of the spirononatriene.

(12) (a) Alfred P. Sloan Fellow, 1963–1967. (b) Gulf Oil Fellow, 1966–1967.

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Reversible Combination of Molecular Nitrogen with a Cobalt Complex. Exchange Reactions of Nitrogen–Tris(triphenylphosphine)cobalt with Hydrogen, Ethylene, and Ammonia

Sir:

Previously we reported that molecular nitrogen combines with a cobalt complex in the reaction of cobalt acetylacetonate, diethylaluminum monoethoxide, and triphenylphosphine carried out in an atmosphere of nitrogen.[1] We wish to report now on some exchange reactions of the isolated complex, nitrogen–tris(triphenylphosphine)cobalt (I), with molecular hydrogen, ethylene, and ammonia. Recently, ruthenium[2,3] and iridium[4] complexes, which are combined with molecular nitrogen, have been reported, but no report has been made, as far as we know, on the reaction of a nitrogen-coordinated complex with these gases.

When a benzene solution of nitrogen–tris(triphenylphosphine)cobalt (I) is swept or shaken with purified hydrogen gas, the original red color changes to yellow with a loss of molecular nitrogen from the complex, as proved by infrared and mass spectrometry. The sharp strong band at 2088 cm^{-1} assigned to the stretching vibration of the coordinated nitrogen molecule disappears rapidly with the appearance of new bands at about 1940 and 1760 cm^{-1}. Sweeping the benzene solution of I with argon gas does not affect the original spectrum at all. On concentrating the yellow benzene solution, light yellow crystals are isolated which can be recrystallized from toluene. *Anal.* Calcd for $C_{54}H_{47}P_3Co$ (II): C, 76.50; H, 5.59. Found: C, 76.72; H, 6.00; N, 0. Thermal decomposition of the yellow complex II releases hydrogen and benzene. On sweeping the yellow solution of II with nitrogen, the ν_{N_2} band at 2088 cm^{-1} resumes the original intensity and the solution regains its initial red color. The cycle can be repeated many times, showing a reversible equilibrium.

$$\underset{\text{I}}{[(C_6H_5)_3P]_3Co\cdot N_2} + H_2 \rightleftarrows \underset{\text{II}}{[(C_6H_5)_3P]_3CoH_2} + N_2 \qquad (1)$$

On sweeping the benzene solution of I with deuterium, a band is observed at 1260 cm^{-1} which may be assigned to a Co–D stretching vibration which is shifted from the band of Co–H stretching vibration at 1760 cm^{-1} by a factor of 1.4. The band at 1940 cm^{-1} was not observed in the spectrum of the benzene solution swept with deuterium, but no corresponding new band due to deuterium substitution appeared. The origin of the band at 1940 cm^{-1} is not clear at the moment.

When a benzene solution of I is swept with purified ethylene, the original red color darkens with the loss of the coordinated nitrogen molecule. The ν_{N_2} band at 2088 cm^{-1} disappears and new bands, which may be assigned to the C–H stretching vibration of the coordinated ethylene molecule, appear at about 2950 and 2850 cm^{-1}. Similar bands are observed in the spectrum of $[(C_6H_5)_3P]_2Ni\cdot C_2H_4$ prepared according to Wilke and Hermann.[5] On passing nitrogen through the solution, these bands disappear and the ν_{N_2} band resumes the original intensity, suggesting a reversible exchange reaction of the type

$$\underset{\text{I}}{[(C_6H_5)_3P]_3Co\cdot N_2} + C_2H_4 \leftrightarrows \underset{\text{III}}{[(C_6H_5)_3P]Co\cdot C_2H_4} + N_2 \qquad (2)$$

Tris(triphenylphosphine)cobalt coordinated with ethylene (III) can be isolated by the reaction of cobalt acetylacetonate, triphenylphosphine, and diethylaluminum monoethoxide in an argon atmosphere.[6] Combination of nitrogen with cobalt also takes place in the reaction of tris(triphenylphosphine)methylcobalt[1] with nitrogen gas.

Analogous reversible reaction of the nitrogen–cobalt complex is observed with ammonia as indicated by the reversible change of the ν_{N_2} band. The complex reacts irreversibly, however, with carbon monoxide and carbon dioxide. The details will be reported later.

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(1) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967).

(2) A. D. Allen and C. V. Senoff, *ibid.*, 621 (1965).

(3) A. E. Shilov, A. K. Shilova, and Yu. G. Borodko, *Kinetika i Kataliz*, 7, 768 (1966).

(4) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **88**, 3459 (1966); **89**, 169 (1967); **89**, 844 (1967).

(5) G. Wilke and G. Hermann, *Angew. Chem.*, **74**, 693 (1962).

(6) Unpublished results.

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Reaction of Benzyne with Benzene. Effect of Silver Ion

Sir:

The decomposition of suspensions of benzenediazonium-2-carboxylate (**1**) in excess benzene at 45° is reported[1] to yield benzobarrelene (**2**), benzocyclooctatetraene (**3**), and biphenyl (**4**) (*cf.* run 8, Table I). The products were postulated to occur by 1,4 addition,[1] 1,2 addition (followed by valence bond isomerism),[1] and insertion[2a] reactions of benzyne (from **1**) on benzene, respectively. These are the "accepted" prod-

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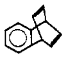
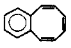
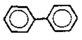
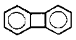
(1) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).

ucts and reaction paths.[2] However, if benzenediazonium-2-carboxylate (**1′**), prepared directly from anthranilic acid and amyl nitrite,[3] is similarly decomposed, the reaction products[4] are **2** and biphenylene (**5**), accompanied with only *trace* amounts of **3** and **4** (run 1). These results are all the more unusual inasmuch as it has been shown[5] that benzyne generated from several different sources appears to behave the same.

The essential difference between **1** and **1′** is that **1** is prepared in a silver ion environment[1] and **1′** is not.[3] The apparent dependence of product distribution on the method of synthesis of benzenediazonium-2-carboxylate is a result of *silver ion contamination*. This was adequately demonstrated (Table I) by decomposing **1′** in benzene, at 45°, containing known amounts of added Ag^+ as the oxide, trifluoroacetate, and perchlorate.[6] The effect of Ag^+ is clearly evident by observing the change in product composition in the absence of added Ag^+ (run 1) to that when the Ag^+:**1′** is $\sim 10^{-9}$ (run 2). By increasing the Ag^+:**1′** to $\sim 10^{-2}$ the amount of **2** formed is reduced to 3.7%.[7]

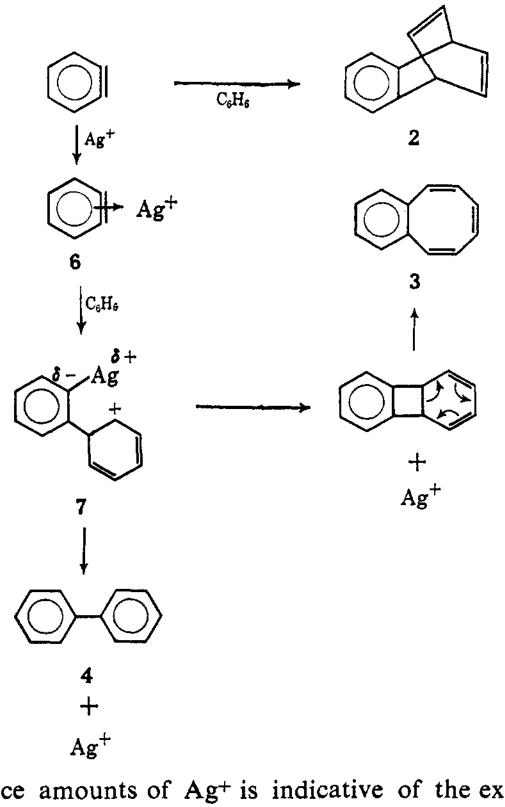
The results from reaction of benzyne with benzene in the presence of Ag^+ are best explained by proposing a benzyne–silver complex (**6**)[8] which would be more electrophilic than benzyne. The complex could attack benzene to give **7** which, by intra- or intermolecular H^+ transfer and ejection of Ag^+, gives biphenyl (**4**) or, by ring closure followed by valence bond isomerism, yields benzocyclooctatetraene (**3**). Thus, the ratio **2**:(**3** + **4**) is a measure of the two competitive processes: (1) 1,4 addition of benzyne to benzene, and (2) benzyne–silver complex (**6**) formation and subsequent reaction with benzene[9] (Scheme I). The magnitude of the effect of trace amounts of Ag^+ is indicative of the extraordinary catalytic ability of Ag^+ to "trap" benzyne and of the reactivity of **6**.

Table I. Decomposition of Benzenediazonium-2-carboxylate (6.7 mmoles) in Benzene (200 ml)[a]

Run[d]	$AgClO_4$, mmoles × 8.5	% compositions[b,c]				$\frac{\mathbf{2}}{(\mathbf{3}+\mathbf{4})}$
						
1	0	88	0.4	1.1	11	59
2	10^{-9}	67	7.9	13	12	3.2
3	10^{-6}	55	13	22	10	1.6
4	10^{-5}	46	17	29	8.4	1.0
5	10^{-4}	17	31	52	0.7	0.2
6	10^{-3}	6.8	35	58	0	0.07
7	10^{-2}	3.7	35	61	0	0.04
8[e]		7.4	44	49	0	0.08

[a] Reaction temperature 45°. [b] Yield of C_{12} hydrocarbons is *ca.* 20%. [c] Hydrocarbons separated on 10 ft × 0.25 in. o.d. 20% SE 30 on Chromosorb W 60–80 mesh, column 135°. Relative retention time: **2**, 0.75; **3**, 0.89; **4**, 1.00; **5**, 1.37; acenaphthene, 1.60 (internal standard). [d] Typical data. [e] Benzenediazonium-2-carboxylate prepared as described in ref 1.

Scheme I



In the "complete" absence of Ag^+, benzyne reacts with benzene to give benzobarrelene by 1,4 addition.[10]

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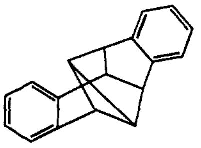
(2) *E.g.:* (a) E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965); (b) S. F. Dyke, A. R. Marshall, and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966).

(3) Amyl nitrite (5 ml) was added to a solution of anthranilic acid (3.0 g) and trifluoro- or trichloroacetic acid (0.03 g) in THF (30 ml). After 1–1.3 hr the mixture is cooled to ~10°, and the off-white to pale yellow solid is collected and washed with THF until washings are colorless, and then with benzene. The yield of **1′** varies between 92 and 95%. *Dry* **1′** *is exceedingly hazardous.* Solvent (benzene) moist material (much less hazardous) was used in this study.

(4) Several other hydrocarbons are formed in this reaction. A major product, $C_{18}H_{14}$, mp 154–155° (6–10% yield), was identified (on the basis of its nmr spectrum) as hexacyclo[$8.7.1.0^{2,7}.0^{8,17}.0^{11,16}$]octadeca-2,4,6,11,13,15-hexaene (i). From reaction of **1′** with **2** in refluxing



i

ethylene chloride i was prepared in >80% yield. This compound was also discovered in Professor Stiles' laboratory (M. Stiles, U. Burckhardt, and G. Freund, *J. Org. Chem.*, in press). The structure of i was confirmed by an X-ray crystallographic study: J. W. Schilling and C. E. Nordman, American Crystallographic Association Meeting, Atlanta, Ga., Jan 1967, Abstracts, p 22.

(5) R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1017 (1963).

(6) The ratio of **3**:**4** is somewhat dependent of the anion, but not that of **2**:(**3** + **4**). Compare **3**:**4** = 0.9 from run 8 which appears to be contaminated with about 0.1% Ag^+ as AgCl and/or Ag_2O with that of ~0.6 from runs 2–7 containing $AgClO_4$. This will be discussed in detail in the full paper.

(7) (a) **2**, **3**, **4**, and **5** are not interconverted nor destroyed by the action of Ag^+. (b) 1,4 Addition seems to be the usual reaction path of arynes with arenes. *Cf.* Reaction of tetrachlorobenzyne (from the Grignard reagent) and mesitylene (H. Heany and J. M. Jablonski, *Tetrahedron Letters*, 4529 (1966)); formation of dibenzobarralene in 30% yield from **1′** and 2 equiv of naphthalene (this study) or from **1** and excess naphthalene in 7% yield;[1] ring A adducts (1,4) from benzyne and anthracenes (G. H. Klanderman, *J. Am. Chem. Soc.*, **87**, 4649 (1965)). 4-Me-**1′** behaves similarly.

(8) Structures can be drawn which involve overlap of d orbitals of Ag^+ with the sp^2 orbitals and/or with the benzene π systems. For examples of silver olefin and silver dialkylacetylene complexes see F. R. Hapner, K. N. Trueblood, and H. J. Lucas, *ibid.*, **74**, 1333 (1952); A. E. Comyns and H. J. Lucas, *ibid.*, **79**, 4339, 4341 (1957), and references contained therein.

(9) The distribution of the isomeric methylbiphenyls formed from **1′** and toluene in the presence of Ag^+ should either support or vitiate the proposed mechanism.

(10) (a) Pyrolysis of phthalic anhydride in benzene-d_6 at 690° gave a mixture of C_{12} hydrocarbons in 48% yield (*based* on unrecovered phthalic anhydride) which consisted of biphenyl-d_6 (from benzyne and benzene!) (~9.4%), naphthalene-d_4 (~81%), acenaphthylene (d_4–d_8 (~6%), and acenaphthene (d_5–d_8) (~5%). In addition extensive

That biphenylene (**5**) is a result of benzyne dimerization was assured since **5** obtained by decomposing **1′** in excess benzene-d_6 was found to be deuterium free, *m/e* 152, C–D stretch absent in the infrared.

None of the other metal ions (Tl^+, Cu^+, Cu^{2+}, Hg_2^{2+}, Hg^{2+})[11] screened thus far altered the course of the benzyne–benzene reaction. The study is being extended however, to transition metals and their complexes in anticipation that an isolable benzyne complex may result.[12]

amounts of biphenyl-d_{10} were formed *via* benzene-d_6 thermal dimerization;[10b] biphenyl-d_6:biphenyl-d_{10} ~0.1. Biphenylene was not detected. Acenaphthylene and acenaphthene are formed *only* by thermal rearrangement of **3**. Based on *isolated* and *characterized* hydrocarbon products, it can be concluded that at 690° the major reaction of benzyne with benzene is 1,4 addition (~75%) to give **2**, followed by loss of acetylene to give thermally stable naphthalene. The balance is electrophilic attack (*vide supra*) to give **4** (~10%) and **3** (~15%) (which rearranges (60%) to form acenaphthene, which in turn is partially dehydrogenated to acenaphthylene) and pyrolysis (40%) to naphthalene. These results are somewhat different from earlier reports[2a] (D. F. Lindow, unpublished data). (b) *Cf.* G. M. Badger, *Progr. Phys. Org. Chem.*, 3, 1 (1966).

(11) The absence of any effect is a strong argument against benzyne attacking a benzene–metal complex.

(12) The assistance of L. R. Rice and D. F. Lindow in carrying out some of the initial experiments is gratefully acknowledged.

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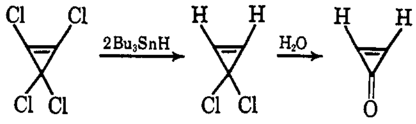
Cyclopropenone

Sir:

Studies of various cyclopropenones, including diphenylcyclopropenone,[1] the earliest example, and the more recent monoalkylcyclopropenones,[2] have fully established the unusual stability of this strained system. Most chemical properties of importance have also been investigated on these derivatives.[1-3] However, although the parent ketone III is clearly of interest, it has resisted our synthetic attempts to prepare it by the methods used to make substituted derivatives. We have now succeeded in synthesizing unsubstituted cyclopropenone.

Reaction of tetrachlorocyclopropene[4] (I) with 2 equiv of tri-*n*-butyltin hydride at room temperature in paraffin oil produced a volatile mixture[5] of chlorocyclopropenes containing 3,3-dichlorocyclopropene (II) (nmr: δ 8.0), 1,3-dichlorocyclopropene (δ 7.2, 4.5, J_{AB} = 2 cps), and mono- and trichlorocyclopropene isomers. The distilled mixture was taken up in CCl_4 and cautiously hydrolyzed with cold water (or D_2O). The aqueous phase contained as the only detectable signal (the solvent peak could be moved by adding potassium phosphate or removed by using D_2O) a sharp singlet at δ 9.0 which we assign to the protons of cyclopropenone (III).



I II III

The nmr spectrum unambiguously establishes this structure. Thus the singlet shows ^{13}C satellites with the very large coupling ($J_{^{13}C-H}$ = 230 cps) characteristic of a cyclopropene[6] or acetylene. The latter is, of course, excluded by the chemical shift of δ 9.0; this also excludes nonketonic cyclopropene structures since 1,3,3-trimethylcyclopropene has its vinyl proton at δ 6.7 and the 3,3-dichlorocyclopropene signal is at δ 8.0, while methylcyclopropenone is at δ 8.7. The ^{13}C satellites of III appear, as expected, as a doublet (J_{H-H} = 3 cps).

The aqueous solution of III shows broad infrared absorption centered at 1850 cm^{-1}. On standing it slowly ($t_{1/2}$ at 25° >1 week) is hydrolyzed to acrylic acid.[8] Treatment with alkali produces a dark polymer, but the compound is stable to a variety of strong mineral acids. Although III is very polar, it can be extracted from the water solution with methylene chloride or ethylene chloride by salting out. The protons in III are still at δ 8.9–9.0, there are no other signals in the nmr, and the infrared spectrum shows a strong cyclopropenone doublet[9] at 1835 and 1870 cm^{-1} and no absorption in the O–H region. Thus III is apparently present as the free ketone, rather than a *gem*-diol, even in aqueous solution.

Attempts to isolate III by removal of solvent, distillation, or vapor phase chromatography under a variety of conditions have so far failed, leading to at least partial polymerization of the compound; the parent ketone is apparently more sensitive than its derivatives. However, the low reactivity of III compared with cyclopropanone,[10] and in particular its retention of the unhydrated carbonyl group in water solution, confirm our previous conclusion that the cyclopropenone system has considerable conjugative stabilization.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health, and thank Mr. John Groves for several experimental contributions.

(1) R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959); M. E. Vol'pin, Y. D. Koreshkov, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, 506 (1959); R. Breslow, T. Eicher, A. Krebs, R. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1320 (1965).

(2) R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966).

(3) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965).

(4) S. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2481 (1966).

(5) Although the allylic chlorines must be most reactive, the resulting conjugated cyclopropenyl radical may pick up hydrogen on any ring position and the cyclopropenyl chlorides undergo rapid allylic isomerizations. Under appropriate conditions the essentially pure mixture of dichlorides can be prepared. On treatment with $AgBF_4$ in a variety of solvents Mr. John Groves has found that this affords chlorocyclopropenium ion, with an nmr singlet at δ 9.6 ($J_{^{13}C-H}$ = 242 cps, J_{H-H} = 2 cps).

(6) Methylcyclopropenone[2] has $J_{^{13}C-H}$ = 213 cps and 1,3,3-trimethylcyclopropene[7] has $J_{^{13}C-H}$ = 218 cps.

(7) G. L. Closs, *Proc. Chem. Soc.*, 152 (1962).

(8) Identified by comparison of vpc, nmr, and mass spectra with those of an authentic sample.

(9) The spectra in aqueous and nonaqueous solution mirror those for alkylcyclopropenones[2] and indicate that the carbonyl group is still present in water, albeit hydrogen bonded.

(10) N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966).

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Singlet Oxygen Reactions from Photoperoxides

Sir:

It has been known for some time that aromatic hydrocarbons such as anthracene, rubrene, and tetra-