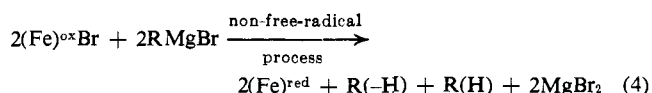
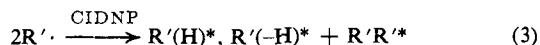
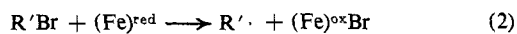


The mechanism in Scheme II is consistent with the

Scheme II



above conclusions.

In this mechanism a reduced iron species (Fe^{red}) reacts with the alkyl halide to form a free alkyl radical and an oxidized iron species (reaction 2). The free alkyl radicals can then diffuse together⁸ and react to produce the polarized disproportionation or coupling products⁹ (reaction 3). Finally the oxidized iron species is reduced by the Grignard reagent (reaction 4) to re-form the catalytically active iron species and hydrocarbons by a non-free-radical route.

Scheme II is similar to the mechanism for the Kharasch reaction suggested by Tamura and Kochi² in which reactions 2 and 4 proceed *via* the intermediacy of organoiron compounds.¹⁰ Our results show, however, that the Grignard reagent and halide must produce different organoiron intermediates, if they are indeed formed, and that the intermediate formed from the Grignard reagent apparently does not decompose homolytically, as has been suggested for organocobalt reagents produced from Grignard reagents.¹¹

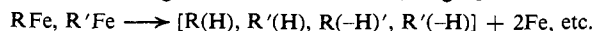
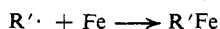
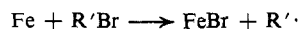
An exception to the above mechanism appears to occur when the halide or Grignard can produce an especially stable radical. We have found, for example, that *tert*-butyl Grignard reacts with allyl and benzyl bromides in the absence of catalyst. The polarizations in these two systems, however, indicate a mechanism in which geminate radical pairs form *via* bimolecular reactions of the organomagnesium compound and halide (as is the case for the reactions of organolithium and halides).⁵

Work is presently underway to determine whether other catalysts such as cobalt or silver salts also produce separate reaction pathways for the Grignard reagent and halide.

(8) A paramagnetic iron-containing species, which might be a likely partner in a radical pair, would probably have a *g* factor different from that of an alkyl radical and be expected to product net enhancement,⁶ rather than the observed multiplet effect, in reaction products.

(9) Reaction of 1 mol each of Grignard reagent and alkyl halide produces 0.08 mol (8% yield) of 2,3-dimethylbutane. This is considerably lower than the 35% yield reportedly obtained from two isopropyl free radicals generated by photolysis of diisobutryl peroxide [R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970)]. If, however, it is assumed that the coupling product is formed exclusively from free radicals derived from the alkyl halides, *i.e.*, that the Grignard reagent forms intermediates which give only propene and propane, the calculated yield is 16%. Although this is still low, the difference lies within the range of medium effects on coupling-disproportionation ratios [A. Stefani, *J. Amer. Chem. Soc.*, **90**, 1694 (1968)] and probably makes it unnecessary to postulate more than one pathway for reaction of the alkyl halide in this case, although a competitive pathway involving organoiron intermediates derived from the halide could also account for the results.

(10) The specific mechanism is shown below.



(11) A summary of the various mechanisms proposed for the Kharasch reaction is presented by M. H. Abraham and M. J. Hogarth, *J. Organometal. Chem.*, **12**, 497 (1968).

Acknowledgments. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society. H. R. W. is pleased to acknowledge a most helpful discussion with Professor H. O. House and correspondence with Professor J. K. Kochi.

(12) Alfred P. Sloan Research Fellow, 1969–1971.

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Oxidative Photoaddition of *p*-Benzoquinone to Cyclooctatetraene. A Chemical Application of the Laser

Sir:

During the course of an exploratory investigation intended to appraise the photochemical potential of the laser, we have studied the photocycloaddition of *p*-benzoquinone to cyclooctatetraene (COT).¹ A 6-W argon ion laser was used to selectively promote the *p*-benzoquinone to its n, π^* excited state.² The ensuing photochemistry has been observed to be profoundly influenced by solvent acidity and the presence of oxygen.

In the absence of oxygen, irradiation of COT and *p*-benzoquinone affords a single product (1) (Scheme I). This sensitive substance is apparently the same as the material previously observed,¹ except that in this instance it could be readily isolated in crystalline form, mp 67–72° dec, from the uncomplicated laser reaction mixture. The adduct exhibits two single proton triplets in the nmr [δ 2.74 ppm ($J = 8$ Hz) and 4.67 ppm ($J = 5$ Hz)], which are not coupled to each other. Hydrogenation (Pd/C) of this adduct yields a phenolic alcohol 2, mp 136.8–137.2°, which is not the same as the phenolic alcohol 3, mp 120–121°, obtained from the hydrogenation (Pd/C) of the oxetane derived from cyclooctene and *p*-benzoquinone. These data together with the further chemistry of 1, *vide infra*, strongly suggest that this substance is the 1,4-adduct 1 and not the 1,2-adduct 4 as proposed originally.³ Irradiation of COT and *p*-benzoquinone in acetic acid either in the presence or absence of oxygen leads to two new substances as the only products: 5 [oil; nmr (60 MHz) δ 2.02 (s, 3 H), 2.30 (q, 1 H, $J = 6$ Hz), 5.42 (m, 2 H), 6.22 (m, 2 H), and 6.65 (m, 8 H)] and 6 [mp 81.5–82.5°, nmr (60 MHz) δ 5.48 (d, 1 H, $J = 7$ Hz), 6.48 (d, 1H, $J = 7$ Hz), and 6.65–7.75 (m, 10 H)]. These same materials are formed when the adduct 1 is warmed in acetic acid. Prolonged heating results in the complete conversion of both 1 and 5 to 6. Similar acid catalyzed rearrangements have been observed with the epoxide of COT and certain cycloheptatriene derivatives.⁴

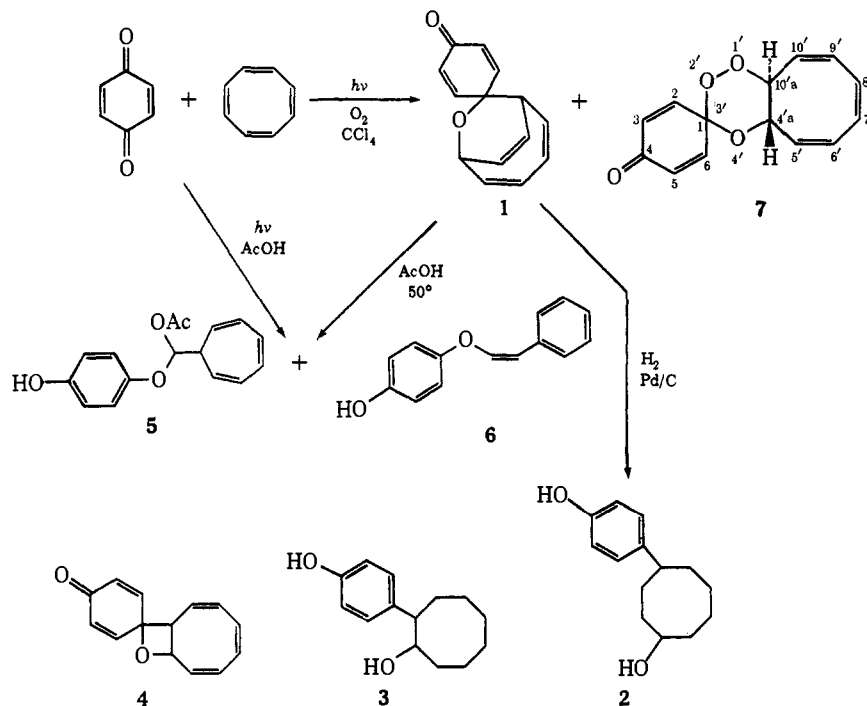
(1) D. Bryce-Smith, A. Gilbert, and M. G. Johnson, *J. Chem. Soc. C*, 383 (1967).

(2) A Coherent Radiation Model 53A argon ion laser with lines at 514.5 nm (2.5 W), 501.7 (0.5), 496.5 (0.7), 488.0 (1.5), 476.5 (0.6), and 457.9 (0.2) was used. At these wavelengths COT has an extinction coefficient of approximately $\epsilon 10^{-5}$, and *p*-benzoquinone has λ_{max}^{hexane} 458 nm ($\epsilon 21$) and 479 ($\epsilon 11$).

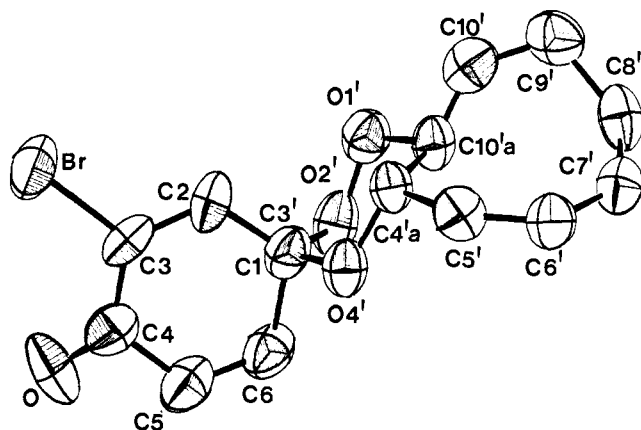
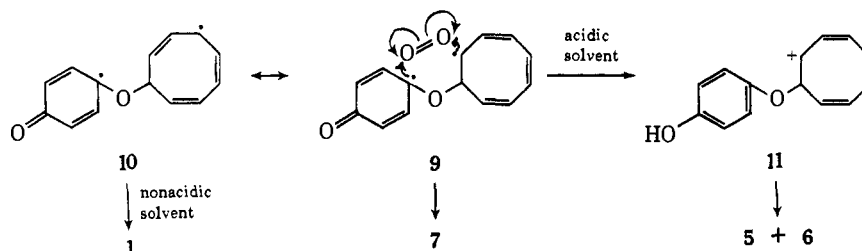
(3) In the photoaddition of quinone carbonyls to conjugated dienes, 1,4 addition appears to be favored over the more usual 1,2 addition: J. M. Bruce, *Quart. Rev. Chem. Soc.*, **21**, 405 (1967).

(4) C. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 576 (1958).

Scheme I



Scheme II

Figure 1. The stereochemistry of **8**.

Of particular interest is the observation of yet another substance as the major product (49%) formed along with **1** (31%) when COT and *p*-benzoquinone are irradiated in nonacidic solvents and in the presence of oxygen. This substance has mp 111.7–111.9°; ir (KBr) 1670 and 1635 cm^{-1} ; nmr (90 MHz, CCl_4) δ 4.88 (m, 2 H), 5.70 (bt, 2 H), 6.13 (m, 4 H), 6.25 (dd, 1 H, $J = 10.8, 2$ Hz), 6.30 (dd, 1 H, $J = 10.4, 2$ Hz), 6.58 (dd, 1 H, $J = 10.4, 3.1$ Hz), 7.62 (dd, 1 H, $J = 10.8, 3.2$ Hz); m/e 244; positive starch-iodide test for peroxide. Structure **7** is consistent with these data

which suggest a COT:*p*-benzoquinone: O_2 dienone-peroxide adduct. Since it was not possible to verify this structure using a degradative chemical approach, a single-crystal X-ray study was conducted using a monobromo derivative **8** prepared from **7** with pyridinium hydrobromide perbromide; **8** had mp 138.8–139.1°; nmr (60 MHz) δ 4.82 (m, 2 H), 8.00 (d, 1 H, $J = 2$ Hz).

The X-ray intensity data were collected for 4059 reflections with a Syntex PI automatic diffractometer using Mo $K\alpha$ radiation. The structure has been solved by heavy atom methods, and at the present stage full-matrix, least-squares refinement (anisotropic temperature parameters) has led to a crystallographic R factor of 0.073. These data confirm the structure of 3-bromo-4',10'-dihydrospiro[2,5-cyclohexadiene-1,3'-cycloocta-*as*-trioxin]-4-one (**8**) (Figure 1), and the parent trioxane **7**.⁵ The data also display the trans ring fusion at carbon atoms 4'a and 10'a as well as the rigid chair conformation of the trioxane ring with the bromine atom situated on the axial half of the dienone system. The peroxide linkage is 1.49 (1) Å as compared with the hydrogen peroxide bond distance of 1.48 Å,⁶ while the dihedral $C3'-O2'-O1'-C10'a$ angle is 111 (2)°. It should also be noted that the spiro carbon atom has significant deviation from typical tetrahedral angles:

(5) We are indebted to K. L. Loening of Chemical Abstracts Service for suggesting this nomenclature.

(6) L. S. Silbert, "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, Table 1, p 649.

$\angle O2'-C$ spiro- $O4'$, 109 (1)°; $\angle O2'-C$ spiro- $C6$, 104 (1)°; $\angle C2-C$ spiro- $C6$, 117 (1)°; $\angle C2-C$ spiro- $O4'$, 109 (1)°.

A single example of this type of oxidative photoaddition has been observed in the photooxidation of a plastoquinone model system.⁷ The most appealing of several plausible mechanisms for the formation of these trioxanes is outlined in Scheme II. The attack of an n, π^* state of *p*-benzoquinone upon COT should lead to the triplet diradical species $9 \leftrightarrow 10$, which would presumably have a significant lifetime before spin inversion made possible collapse to the 1,4-adduct **1**. If this triplet species has a sufficiently long lifetime,⁸ it might be trapped by molecular oxygen to form the 1,2,4-trioxane **7**. Since molecular oxygen exists as a ground state triplet, it is conceivable that this trapping might proceed in a concerted fashion and might be viewed as a form of triplet-triplet annihilation. Both **7** and **1** are stable under the irradiation conditions in acetic acid, and yet neither of these products is observed in this solvent. The absence of **7** might be indicative of a reduced lifetime of $9 \leftrightarrow 10$ in acidic media, and the absence of **1** might indicate that protonation also alters the mode of collapse of $9 \leftrightarrow 10$ in such a way as to form **5** and **6** directly. Perhaps this occurs through the ion **11**.

Finally, it should be noted that these reactions are not the results of some exotic property of the laser radiation. However, products such as **7** cannot be prepared in more than trace amounts with the more usual near-ultraviolet light sources, since they are destroyed nearly as fast as they are formed. Filtered sources may be used, but then the light intensity can be so drastically attenuated that the accumulation of appreciable amounts of product can require long irradiation times. Under these conditions **1** and **7** can undergo significant decomposition which greatly hampers their isolation. Thus, a laser light source, while not essential to an investigation of this nature, simplifies the task considerably.

A full account of this and related work will be forthcoming.

Acknowledgments. We express our appreciation to the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work, to Mr. Robert J. Weber, Jr., for his able laboratory assistance, and to Badische Anilin und Sodafabriken for their most generous gift of COT.

(7) D. Creed, H. Werbin, and E. T. Strom, *J. Amer. Chem. Soc.*, **93**, 502 (1971).

(8) J. A. Barltrop and B. Hesp, *J. Chem. Soc.*, 5182 (1965).

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Received October 27, 1972

—E Mass Spectra

Sir:

We describe a new type of mass spectrum which is the result of converting positively charged to negatively charged ions in the analyzer of the mass spectrometer. Preliminary results suggest that these mass spectra may be valuable in characterizing the structures of both positively and negatively charged ions.

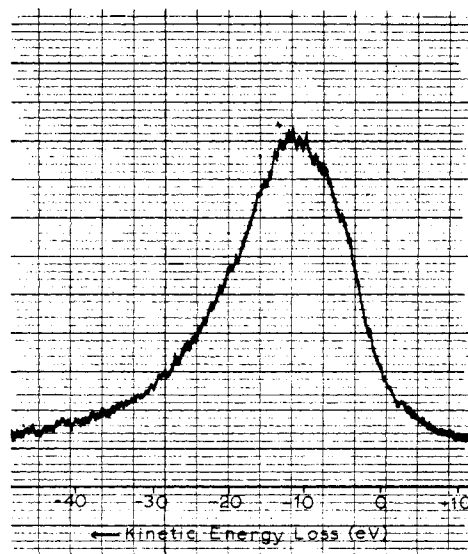
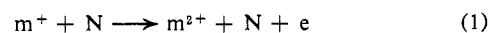
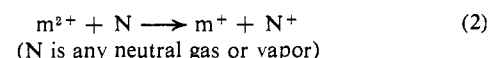


Figure 1. Kinetic energy spectrum of the beam of negatively charged ions generated from positively charged benzene ions (energy 8 keV) by collision with benzene vapor.

In earlier work we have employed high-energy (keV) ion-molecule reactions occurring in the analyzer of the mass spectrometer to effect charge stripping¹ (1) and



charge exchange² (2). These two reactions can be used



to provide a wealth of information on the internal energies of ions, on thermochemical quantities such as double ionization potentials, and on ion-molecule reaction mechanisms at high energy.³ Moreover, reactions 1 and 2 each form the basis for a new type of mass spectrum, $E/2$ and $2E$ mass spectra,⁴ respectively. The analytical potential of doubly charged ion mass spectra ($2E$ spectra) has already been explored in some detail² and $E/2$ spectra are under study in this regard.

Consider a double-focusing mass spectrometer of Nier-Johnson geometry⁵ operated at ion accelerating voltage V and electric sector voltage E and equipped with a detector at the point of energy focus, *i.e.*, between the electric and magnetic sectors. If the polarities of the electric sector plates are reversed (the $-E$ condition) but all other voltages left unchanged, then only negatively charged ions of kinetic energy eV will be transmitted by the electric sector and detected. Moreover, all such negatively charged ions must have been generated from positively charged ions in the field-free region preceding the electric sector. Figure 1 shows the kinetic energy distribution of the negatively charged ions

(1) (a) R. G. Cooks, J. H. Beynon, and T. Ast, *J. Amer. Chem. Soc.*, **94**, 1004 (1972); (b) T. Ast, J. H. Beynon, and R. G. Cooks, *ibid.*, **94**, 6611 (1972).

(2) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 455 (1970); (b) J. H. Beynon, A. Mathias, and A. E. Williams, *ibid.*, **5**, 303 (1971); (c) T. Ast, J. H. Beynon, and R. G. Cooks, *ibid.*, **6**, 741, 749 (1972).

(3) J. H. Beynon, R. M. Caprioli, R. G. Cooks, and G. R. Lester, "Metastable Ions," Elsevier, Amsterdam, in press.

(4) So called because the electric sector in a double-focusing mass spectrometer is operated respectively at one-half and twice the potential (E) normally used to obtain mass spectra.

(5) Our experiments were done using the Hitachi RMH-2 mass spectrometer, modified as previously described.^{1b}