Ketone **4a** was prepared from 2-cyclopentenone by photocycloaddition with 1,2-dichloroethylene, ketalization, dehalogenation, hydrogenation, bromination, dehydrobromination, and hydrolysis[5] in an overall yield of 47%.[6] 7-Ketonorbornene, **6a**, was identified by comparison of infrared and nmr spectra with those of authentic material.[7,8] The synthesis of *exo*-6,7-bisdeuteriobicyclo[3.2.0]hept-3-en-2-one, **4b**, was accomplished as outlined above except that reduction with deuteriodiimide[10] was substituted for the hydrogenation step. Irradiation of **4b** as above gave 5,6-bisdeuterio-7-ketonorbornene.

Because of the simplicity of the nmr spectra of 7-ketonorbornenes,[11] determination of the stereochemistry of the allylic rearrangement is simply a matter of measuring the ratio of *endo* and *exo* protons in the dideuterated product.[12] The nmr spectrum of labeled 7-ketonorbornene obtained from irradiation of **4b** exhibits signals at δ 1.90 and 1.13 corresponding to the *exo* and *endo* protons, respectively, on C-5 and C-6. The integrated area of the lower field signal is 2.5 times that of the upfield one, indicating that the photochemical isomerization, **4** → **6**, proceeds with complete loss of stereochemistry at the migrating carbon.[13]

In order to eliminate loss of stereochemical integrity in ketone **4** *via* rapid equilibration with diradical **5** followed by a slower concerted isomerization of **4** to **6** as a possible course of events, we determined the stereochemistry of product and of recovered starting ketone both after *ca.* 70 and 25% disappearance of starting ketone **4**. The stereochemistry of product ketone, **6**, as determined by the nmr analysis outlined above, was invariant with reaction progress. Starting ketone, **4b**, underwent loss of stereochemistry at one of the labeled carbons, presumably C-6, relatively slowly; the stereomutation was *ca.* 50% complete at 25% reaction.

In a final control experiment, irradiation of *cis*-*exo*-5,6-dideuterio-7-ketonorbornene, **6d**,[14] under the conditions of the isomerization (0.040 *M* in pentane) gave only recovered material with no loss of stereochemistry, nor was decarbonylation observed.[15]

The experimental results outlined above clearly demonstrate the nonconcerted nature of the isomerization, **4** → **6**, and imply that the verbenone–chrysanthenone isomerization is likewise nonconcerted. The intermediacy of diradical **5** is strongly indicated.[16]

That the isomerizations reported here are nonconcerted does not detract from the theory of orbital symmetry conservation in concerted reactions, but serves to emphasize that relaxation of electronically excited species to ground-state diradicals is often the major path in photochemical reactions.

---

[5] This sequence is a combination of methods first described by H. O. House and T. H. Cronin, *J. Org. Chem.*, 30, 1061 (1965), and E. W. Garbish, *ibid.*, 30, 2109 (1965).

[6] Satisfactory combustion analyses as well as nmr, ir, and uv spectra of all new compounds and/or suitable derivatives thereof have been obtained.

[7] We thank Professor R. S. Bly for this comparison.

[8] The synthesis of **1** was similar to that of **4a**. See also R. L. Cargill, A. C. Miller, D. M. Pond, P. deMayo, M. F. Tchir, K. R. Neuberger, and J. Saltiel, *Mol. Photochem.*, **1**, 301 (1969). The structure of **2** rests on the spectral data, $\lambda_{\max}^{\mathrm{EtOH}}$ 270 nm (ϵ 21), $\bar{\nu}_{\max}^{\mathrm{CCl_4}}$ 1665 and 1785 cm^{-1}. The nmr spectrum exhibits a signal at 6.00 ppm (single vinyl hydrogen). Thermal decarbonylation to the known diene, **3**,[9] completes the structure proof.

[9] R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, **85**, 3030 (1963). We thank Professor Bates for comparing the spectra of our diene with those of his sample.

[10] Exclusive *exo* deuteration was established by analysis of the 60- and 100-MHz nmr spectra of **4b**. The deuterium content of **4b** was determined by nmr and mass spectrometry to be 87% d_2, 10% d_1, and 3% d_0. We thank Professor P. G. Gassman for his advice concerning the deuteriodiimide reduction.

[11] The nmr spectra of norbornenes are discussed by A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, **90**, 3724 (1968), and by B. Franzus, W. C. Baird, N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968), and references cited therein. A complete analysis of our spectra will be presented in the full paper.

[12] Given the deuterium analysis of **4b**, see ref 10, and making the reasonable assumption that in the monodeuterated species C-6 and C-7 are equally deuterated (*exo*), we may calculate the ratio of *exo* to *endo* protons in the product, **6**, for each of three limiting cases. For rearrangement occurring with complete retention of configuration at the migrating carbon, this ratio will be 12; for migration with complete inversion, 1.0; and for migration with complete loss of stereochemistry, 2.5. It is assumed in these calculations that the stereochemical integrity of C-7 is retained.

[13] From analysis of the deuterium-decoupled 100-MHz nmr spectrum of labeled photoproduct **6**, it is possible to rule out the presence of *cis*-*exo*-5,6-bisdeuterio-7-ketonorobornene (**6d**). A mechanism for isomerization of **4** involving dissociation into ethylene and cyclopentadienone followed by recombination in a Diels–Alder reaction is thereby excluded.

[14] This ketone was prepared from the corresponding alcohol, B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965), by the method of R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).

[15] The photodecarbonylation of **6** and related ketones is discussed by (a) D. I. Schuster, F-T. H. Lee, A. Padwa, and P. G. Gassman, *ibid.*, 30, 2262 (1965); (b) L. D. Hess, Ph.D. Dissertation, University of California, Riverside, Calif., 1965; quoted in J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 407; and (c) J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

[16] It has been noted (ref 2f,g) that when the migrating carbon bears certain substituents, thermal and photochemical allylic shifts occur with loss of stereochemistry. Possible substituent effects on the photochemical isomerizations reported here are eliminated; therefore our results show that the nonconcerted path is the less energetic one for this type rearrangement.

R. L. Cargill, Benjamin M. Gimarc, David M. Pond
Thomas Y. King, A. Bradford Sears
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

M. Robert Willcott
Department of Chemistry, University of Houston
Houston, Texas 77004

Received March 5, 1970

Reaction of Atomic Oxygen with Aromatic Hydrocarbons[1]

Sir:

Reactions of oxygen atoms with organic molecules have been reported by a number of investigators;[2,3] however, reactions with saturated hydrocarbons and aromatic compounds have received little attention, possibly due to the decreased reactivity of these compounds. Using the mercury photosensitized decomposition of nitrous oxide, Cvetanović[4] studied benzene and toluene in a circulating system. Benzene gave phenol while toluene gave three to four times as much *o*-cresol as *p*-cresol and less than 5% *m*-cresol in the volatile addition products.

---

[1] This research was partially supported by a Predoctoral Fellowship from the National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control, Public Health Service, awarded to A. J. M. (F3-AP-35, 476), and by the National Aeronautics and Space Administration, Grant No. NsG-657.

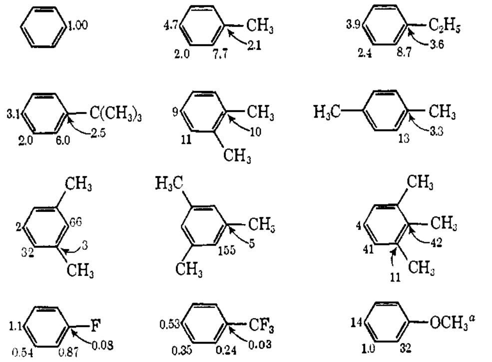
[2] (a) E. Murad and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **81**, 6405 (1959); (b) I. Haller and G. C. Pimentel, *ibid.*, **84**, 2855 (1962); (c) D. Saunders and J. Heicklen, *ibid.*, **87**, 2088 (1965).

[3] R. J. Cvetanović, *Advan. Photochem.*, **1**, 115 (1963).

[4] G. Boocock and R. J. Cvetanović, *Can. J. Chem.*, **39**, 2436 (1961); G. R. H. Jones and R. J. Cvetanović, *ibid.*, **39**, 2444 (1961).

We wish to make a preliminary report on work with ground-state atomic oxygen, O(^{3}P), and aromatic compounds. The oxygen atoms were generated by decomposition of nitrous oxide by mercury atoms which were activated by 2537-Å light from a low-pressure Hanovia mercury-vapor lamp equipped with a Vycor filter. These vapor-phase oxidations utilized a flow system (100–200 ml of N_2O/min) at atmospheric pressure (740 ± 4 Torr) and 30 ± 1°. For twelve of the thirteen aromatic compounds studied, phenolic products accounted for greater than 95% of the volatile addition products;[5] varying amounts of tars were found in every case. Table I gives the partial rate factors relative to benzene as calculated[6] from relative reactivities and product distributions determined by vapor-phase chromatography.

Table I. Partial Rate Factors for Formation of Phenols with Atomic Oxygen at 30°



[a] The partial rate factor for methoxyl cleavage cannot be determined because of concurrent photolysis to yield phenol.

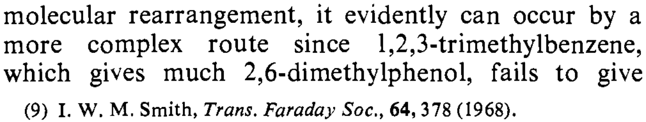
Table I demonstrates the electrophilic character of atomic oxygen, O(^{3}P). The substitution pattern of toluene, other alkylbenzenes, and anisole is similar to that in electrophilic attack by polar reagents;[6] however, the *ortho* positions are more reactive than the *para*[7] as in attack by aryl radicals.[8] A plot of the logarithm of the partial rate factors for attack of atomic oxygen, at the *meta* and *para* positions of the monosubstituted benzenes at 30°, against σ^+ values[6] gives a good Hammett relation (13 points) with ρ equal to -1.15 and a correlation coefficient of 0.95. A somewhat better relation is obtained if the point for the *p*-trifluoromethyl group is omitted (ρ of -1.28 and correlation coefficient of 0.97). The present oxidation has a reaction constant of smaller numerical magnitude than obtained in most electrophilic aromatic substitutions by polar reagents where values of ρ of -2.4 to -12.1 have been reported.[6]

For the polymethylated benzenes the total relative rates of oxidation at all aromatic positions bearing hydrogen have been calculated based on the partial rate factors for toluene and the "additivity principle."[6] Whereas in common electrophilic aromatic substitution such calculations generally give good agreement between calculated and observed values, in the present case the calculated generally exceed the experimental values, such that a plot of log k_{found} (as ordinate) *vs.* log k_{calcd} gives a straight line of slope 0.84 (correlation coefficient 0.98). We believe that the present attenuation in reactivity is a reflection of the very fast rate of reaction of atomic oxygen with aromatic hydrocarbons. Thus benzene[3,9] appears to react with atomic oxygen at 25° at a rate of about $1.2 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, which is only some 10^4-fold less than the expected collision frequency. With good activating groups, if no attenuation in activation per additional substituent was observed, reaction rates exceeding the rate of collision would be expected by the simple additivity principle. The alternative explanation that the decreased activation on polyalkylation is due to steric hindrance is deemed improbable on the basis that toluene, ethylbenzene, and *t*-butylbenzene have similar partial rate factors. Atomic oxygen is evidently a reagent of low steric requirements.

Methyl cleavage, resulting in phenol from toluene, was not reported by previous investigators.[4] We have discovered a related cleavage of ethyl[10] and *t*-butyl groups. These cleavages also seem to reflect electrophilic attack of atomic oxygen upon the aromatic ring since methyl groups, especially *o*-methyl groups, accelerate the cleavage (see especially 1,2,3-trimethylbenzene).

Oxidation of an equimolar mixture of benzene and perdeuteriobenzene under the present conditions, with analysis of the unreacted hydrocarbons and product phenols by mass spectrometry, gave a value for the intermolecular hydrogen isotope effect, k_H/k_D, of 1.14 ± 0.04. This small isotope effect demonstrates that cleavage of the aromatic C–H bond has not occurred appreciably in the rate-determining step of the oxidation. The isotope effect is near that which is thought to be a secondary isotope effect in some common homolytic and heterolytic aromatic substitutions.[11]

The available data are in agreement with the mechanism shown below. This type of mechanism is related to a proposed[3,12] mechanism for reaction of O(^{3}P) with olefins and to one of tentative nature[4] for O(^{3}P) oxidation of benzene. The intermediate diradical presumably (from the spin conservation principle) is in a triplet state. While collapse of the intermediate to give phenol might occur as a simple intramolecular rearrangement, it evidently can occur by a more complex route since 1,2,3-trimethylbenzene, which gives much 2,6-dimethylphenol, fails to give



---

[5] The exception was ethylbenzene for which the yield of phenols was only 82% of the volatile products; the remainder consisted of acetophenone (4.4%), 1-phenylethanol (6.5%), 2-phenylethanol (0.5%), and unknowns.

[6] L. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

[7] In a recent review,[6] only 5 of 54 examples of electrophilic attack upon toluene by polar reagents showed the *ortho* partial rate factor to exceed the *para*; a similar pattern of reactivities holds for ethyl- and *t*-butylbenzene.

[8] R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965).

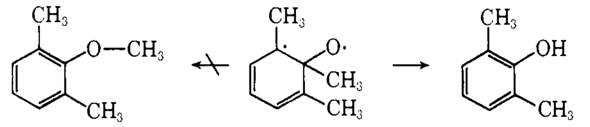
[9] I. W. M. Smith, *Trans. Faraday Soc.*, **64**, 378 (1968).

[10] The faster cleavage of ethyl than of methyl and *t*-butyl may reflect an additional mode of cleavage of ethyl related to the more extensive side-chain oxidation of ethyl.

[11] E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 285 (1964); H. Zollinger, *Advan. Phys. Org. Chem.*, **2**, 195 (1964).

[12] For an alternative more recent mechanism of O(^{3}P) oxidation of olefins see R. Klein and M. D. Sheer, *J. Phys. Chem.*, **73**, 1598 (1969).

appreciable (less than 0.2%) 2,6-dimethylanisole, which might be expected by a simple 1,2 shift of methyl in the intermediate.



Preliminary investigation of nitrobenzene oxidation (at 100°) by the usual Hg-N_2O technique gave 20% phenol and 16% *o*-, 4% *m*-, and 60% *p*-nitrophenol. While such behavior can be rationalized by the known ability[8] of the nitro group to facilitate free-radical attack at the *ortho* and *para* positions, direct photolysis of nitrobenzene[13] under similar conditions in a helium atmosphere gave 28% nitrosobenzene, 51% phenol, and about the same ratio of nitrophenols (4% *o*-, 1% *m*-, and 16% *p*-).

Two chief limitations of the Hg-N_2O technique are formation of tar and direct photolysis. The amount of tar varies with the reactivity of the substrate; the weight ratio of tar to volatile product under comparable conditions was 0.2 for anisole and 2 for benzotrifluoride. The calculation of partial rate factors in the present work presumes that tar formation occurs nonselectively (if at all) from intermediates leading to the phenols. While this assumption has been shown to be valid in the attack of some radicals upon aromatic rings,[14] its application to the present case can be considered justified only by the consistent nature of the results which emerge. Direct photolysis of the substrate occurred with anisole and nitrobenzene; of the halobenzenes, chloro- and bromobenzene give rise to halobiphenyls so readily[15] that only fluorobenzene can be studied by the Hg-N_2O technique.

As far as we are aware, the present work constitutes the most extensive investigation of aromatic substitution in the gas phase. The absence of solvent effects and greater certainty about the identity of the reacting molecules (absence of molecular aggregates) should make this system more amenable to theoretical treatment than liquid-phase aromatic substitutions. In this respect a plot of the logarithm of the partial rate factors, for attack of O(^{3}P) upon nuclear C–H positions on the present alkylbenzenes, gives a fair linear plot *vs.* the ground-state electron density as calculated[16] for individual positions using the CNDO II approximation. This plot implies that the reaction of O(^{3}P) with aromatic hydrocarbons has an early transition state. The correlation further predicts that positions *ortho* to alkyl groups should be more reactive than *para* positions as found. More elaborate calculations involving the oxygen atom would appear worthwhile.

[13] A previous report on photolysis of nitrobenzene listed only nitrosobenzene and *p*-nitrophenol as products: S. H. Hastings and F. A. Matsen, *J. Amer. Chem. Soc.*, 70, 3514 (1948).

[14] D. H. Hey, M. J. Perkins, and G. H. Williams, *Chem. Ind.* (London), 83 (1963); R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, *J. Amer. Chem. Soc.*, **84**, 4152 (1962).

[15] *Cf.* N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Commun.*, 418 (1966).

[16] We are indebted to Mr. John M. McKelvey for assistance in these calculations.

Erling Grovenstein, Jr., Arthur J. Mosher
School of Chemistry, Georgia Institute of Technology
Atlanta, Georgia 30332

Received March 11, 1970

Reactions of Sulfur with Benzylamine[1]

Sir:

Primary amines have been successfully used in the Willgerodt-Kindler reaction[2] where, in addition to normal products, they can lead to novel types of compounds.[3] They have also been used as catalysts in various reactions between elemental sulfur and organic substrates.[4-6] Nevertheless, almost nothing is known of the reaction of sulfur with primary amines.[7,8] We describe here work showing thiodiamines[9] and arylimine polysulfides[10] to be interconverting intermediates in the reaction of sulfur with benzylamine.

With *excess* benzylamine sulfur serves, in an overall sense, as an oxidizing agent. The final products are ammonia, benzylammonium polysulfides, and N-benzylidenebenzylamine, as shown[11] in eq 1 where $x \simeq 6$–7. We propose (eq 2–6) to account for these products[12] where eq 4 is base catalyzed and eq 5 is catalyzed by

$$xS + 4C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}NCH_2C_6H_5 + NH_3 + (C_6H_5CH_2NH_3^+)_2S_x^{2-} \quad (1)$$

sulfide. Pertinent evidence in support of this scheme follows.

$$(a + 1)S + 2C_6H_5CH_2NH_2 \rightleftharpoons H_2S + C_6H_5CH_2NHS_aNHCH_2C_6H_5 \quad (2)$$

$$(x - 1)S + 2C_6H_5CH_2NH_2 + H_2S \longrightarrow (C_6H_5CH_2NH_3^+)_2S_x^{2-} \quad (3)$$

$$3C_6H_5CH_2NHS_aNHCH_2C_6H_5 \longrightarrow C_6H_5CH{=}NS_bN{=}CHC_6H_5 + 4C_6H_5CH_2NH_2 + (3a - b)S \quad (4)$$

$$C_6H_5CH{=}NS_bN{=}CHC_6H_5 + 2C_6H_5CH_2NH_2 \rightleftharpoons 2C_6H_5CH{=}NH + C_6H_5CH_2NHS_bNHCH_2C_6H_5 \quad (5)$$

$$C_6H_5CH{=}NH + C_6H_5CH_2NH_2 \longrightarrow C_6H_5CH{=}NCH_2C_6H_5 + NH_3 \quad (6)$$

The initial steps (reactions 2 and 3) are written based on analogy with previous findings. Tertiary amines (when very pure) are known to be inert to sulfur[7,13] under normal conditions but lead to trialkylammonium polysulfides when hydrogen sulfide is added.[14] Secondary amines react with sulfur to give hydrogen sulfide (isolated as the alkylammonium polysulfide[15]) along

[1] Supported under a grant from the National Research Council, Canada.

[2] M. Carmack, *Org. Reactions*, 3, 83 (1946); F. Asinger and H. Offermanns, "Syntheses mit Ketonen, Schwefel und Ammoniak bzw. Aminen und Chemisches Verhalten der Reaktions Produkte," Opalden, W. Germany, 1966.

[3] F. Asinger and H. Offermanns, *Angew. Chem., Int. Ed. Engl.*, **6**, 907 (1967), and references cited therein.

[4] B. D. Vineyard, *J. Org. Chem.*, 32, 3833 (1967).

[5] G. Petry and W. Scheele, *Kaut. Gummi Kunstst.*, 20, 518 (1967).

[6] F. Asinger, W. Schaefer, and H. Triem, *Monatsh. Chem.*, **97**, 1510 (1966).

[7] R. E. Davis and H. F. Nakshbendi, *J. Amer. Chem. Soc.*, **84**, 2085 (1962).

[8] A. P. Zipp and S. G. Zipp, *Sulfur Inst. J.*, 2 (1968).

[9] Houben-Weyl, "Methoden Organischen Chemie," Vol. XI, Pt. 2, Georg Thieme Verlag, Stuttgart, 1958, pp 744–751.

[10] Y. Sasaki and F. P. Olsen, *Chem. Commun.*, 1424 (1969).

[11] This experimentally verifiable equation is obtained by suitable combination of eq 2–6.

[12] Catenated sulfur species need not be of uniform chain length. The isolated benzylammonium polysulfide averaged about six to seven sulfurs per chain while the arylimine polysulfides appeared mainly with four sulfurs and somewhat less commonly with two or three. No estimate of the sulfur chain length in the thiodiamines is available.

[13] P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Amer. Chem. Soc.*, **83**, 103 (1961); P. D. Bartlett, R. E. Davis, and W. R. Roderick, *ibid.*, **83**, 109 (1961).

[14] H. Krebs, E. F. Weber, and H. Balters, *Z. Anorg. Allg. Chem.*, **275**, 147 (1954).