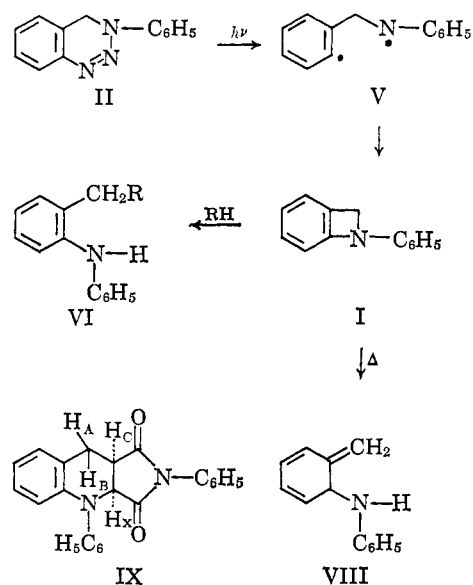


wish to report the isolation and characterization of the stable N-phenylbenzoazetine (I).

3-Phenyl-4H-benzo-1,2,3-triazine (λ_{\max} 360 m μ) (II), derived from the nitrosation of N-(*o*-aminobenzyl)-aniline,⁶ was irradiated in benzene solution with ultraviolet light (Hanovia A 450-w lamp, Pyrex filter) for 30 min at 30° to afford, after chromatography on basic alumina, crystallization from hexane, and sublimation (60°, 10⁻³ mm), a 50% yield of I, mp 104° dec. *Anal.* Calcd for C₁₃H₁₁N: C, 86.19; H, 6.08; N, 7.73; mol wt, 181. Found: C, 85.90; H, 6.02; N, 7.61; mol wt, 170 (cryoscopic in benzene). The ultraviolet absorption occurred with a maxima at 280 m μ . The nmr spectrum of I (CCl₄, 60 Mc) displayed a low-field methylene singlet at τ 5.22 and a nine-proton multiplet from τ 2.7 to 3.4. As anticipated these signals are within the normal aromatic proton envelope and indicate an undisturbed benzenoid ring current.



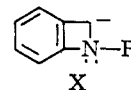
In addition to I the photolyzed solutions of II provided benzalaniline (10%) (III) and 9,10H-phenanthridine (25%) (IV) identified by mixture melting point comparison with authentic samples. The appearance of these products suggests the interposition of a common 1,4-diradical, V, which subsequently undergoes cyclization to I or IV and hydrogen migration to afford III, the reported⁶ product from the thermolysis of II. The long wavelength transition of II may be presumed to arise from the promotion of an antibonding 1,2-aza electron in the higher nonbonding molecular orbital to the π^* configuration.⁷ If the observed transformation occurs in the singlet state, then overlap of the odd electron, coplanar n-orbital with the 2,3- σ bond leads to the generation of an amino and azo radical pair which after loss of nitrogen gives V.⁴

The increased nucleophilic reactivity (*cf.* azetidine³) imposed by the geometry in the base, I, and the corresponding conjugate acid is evident from the following observations. Treatment of I with aniline in benzene at 30° (or more rapidly at 80°) affords in high yield VI

(R = NHC₆H₅), mp 80–81°. Likewise I with acetic acid and sodium acetate in refluxing benzene provided VII (R = OAc), mp 57–58°.⁹

N-Phenylbenzoazetine upon thermal or photochemical excitation is rapidly converted to a reactive species which we propose is the valence tautomer VIII. Photoexcitation (unfiltered radiation from the previously described lamp) in aqueous dimethoxyethane at 30° for 1 hr affords VI (R = OH) isolated as the previously described acetate.¹⁰ This behavior is analogous to the characteristic high nucleophilic reactivity of the related *o*- and *p*-quinone methides. Further evidence for the thermal (200°) production of VIII was provided by its interception with N-phenylmaleimide to yield a 1:1 adduct IX, mp 155–156°. The nmr spectrum (CDCl₃, 60 Mc) of IX displayed an ABCX pattern as a doublet at τ 5.05 for H_X and an octet at τ 6.37 for H_C, reflecting $J_{CX} = 9.5$ cps in agreement with the *cis* relationship of these two protons. A two-proton multiplet at τ 6.97 was assigned to the H_{AB} methylene group and was coupled with H_C in the order $J_{cis} = 6.5$ cps and $J_{trans} = 2.5$ cps.

A study of the chemistry of VIII and the conversion of I or its derivatives to the possibly aromatic anion, X,



is continuing.

Acknowledgment. This investigation was supported by the National Institutes of Health (GM-12672). We also wish to thank Professor John Dyer for assistance in obtaining and analyzing the nmr spectra.

(8) An authentic sample for comparison was prepared by the lithium aluminum hydride reduction of N,N'-diphenylanthranilamide. *Anal.* Calcd for C₁₉H₁₈N₂: C, 83.16; H, 6.62; N, 10.22. Found: C, 82.93; H, 6.65; N, 10.02.

(9) Lithium aluminum hydride reduction of N-phenylanthranilic acid followed by O-acetylation gave an authentic sample of the acetate. *Anal.* Calcd for C₁₅H₁₃NO₂: C, 74.65; H, 6.27; N, 5.81. Found: C, 74.31; H, 6.35; N, 5.79.

(10) It may be noted that I fails to react nonphotochemically with water at 100°.

(11) *Anal.* Calcd for C₂₃H₁₈N₂O₂: C, 77.97; H, 5.08; N, 7.91. Found: C, 77.70; H, 5.10; N, 7.80.

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Reductive Cleavage of Toluenesulfonates with Sodium Naphthalene¹

Sir:

We wish to report that treatment of alkyl toluenesulfonates with sodium naphthalene anion radical in tetrahydrofuran solution constitutes an almost ideal procedure for regenerating the corresponding alcohols. Reconversion of toluenesulfonates to alcohols (O-S cleavage), often a necessary tool for the detailed study of solvolysis reactions, is also important in steroid and carbohydrate chemistry where sulfonate esters are

(1) This work was partially supported by the National Science Foundation, and by the Petroleum Research Fund, administered by the American Chemical Society. We also wish to thank Mr. F. Battaglia, Mr. D. J. Tanner, Mrs. V. Abraitys, and Dr. G. T. Kwiatkowski for experimental assistance.

(6) M. Busch, *Chem. Ber.*, **25**, 445 (1892); *J. Prakt. Chem.*, **51**, 257 (1895).

(7) S. F. Mason, *J. Chem. Soc.*, 1240 (1959).

widely used as protective agents for the hydroxyl group.^{2a}

A typical procedure is to inject a fairly concentrated solution of the toluenesulfonate into a stirred tetrahydrofuran solution containing 2–6 equiv (*ca.* 0.3 *M*) of sodium naphthalene under nitrogen.^{2b} Completion of reaction, indicated by disappearance of the intense green color of the anion radical, usually occurs within a few seconds at room temperature. For certain sulfonates, best yields were obtained by carrying out the reaction at about -80° ; reaction is noticeably slower at this temperature. Addition of a small amount of water to convert the alkoxide salt to alcohol completes the process. (If more than 6 equiv of anion radical is used the color change may not occur; less than 2 equiv may result in incomplete cleavage.) The alcohol may then be isolated by usual techniques such as liquid chromatography or conversion to a suitable derivative and recrystallization. The mixture may also be directly analyzed by gas chromatography after drying with magnesium sulfate. The yield of alcohol, determined by gas chromatography and based on the amount of alkyl toluenesulfonate added, is frequently within experimental error of 100%. In no case was epimerization or other rearrangement of the recovered alcohol observed. While not tested, we feel it unlikely that scrambling of the sulfonate oxygens occurs during the rapid reaction. The speed and ease of this procedure should make it highly recommended. Some typical results are presented in Table I.

Previously reported methods include: reduction with sodium amalgam in ethanol,³ hydrogenolysis with nickel,⁴ and reduction with sodium in liquid ammonia.⁵ Our experience with these techniques indicates that usually they proceed in lower yield than does sodium naphthalene cleavage, and that in sodium-liquid ammonia reduction⁵ epimerization of the resulting alcohol frequently occurs.⁶ In those cases examined, it appears that our method is superior to these.

The mechanism of this reaction is probably similar to that proposed by Kovacs and Ghatak for the sodium-liquid ammonia cleavage of toluenesulfonamides.⁷ At higher concentrations of sodium naphthalene toluene production is substantial (80–90%), while at low concentrations of anion radical (*ca.* 2 equiv) alkoxide formation remains complete, or nearly so, but the yield of toluene is relatively low. Sodium toluenesulfinate does not produce toluene when treated with an excess of sodium naphthalene under these conditions. (Sodium toluenesulfonate *does* yield a modest amount of toluene, but it, of course, is not a likely precursor.)

(2) (a) H. J. E. Loewenthal, *Tetrahedron*, **6**, 269 (1959); R. S. Tipson, *Advan. Carbohydrate Chem.*, **8**, 108 (1953). (b) The sodium naphthalene solution is most conveniently prepared by stirring (with a glass-covered stirring bar) clean pieces of sodium with an equivalent amount or slight excess of naphthalene in dry tetrahydrofuran in a sealed system under an atmosphere of nitrogen or argon for approximately 1 hr at room temperature. Formation of the anion radical appears to be sensitive to traces of oxygen and other impurities, and the time required for complete reaction of the sodium under these conditions is quite variable. Once formed, the anion radical solution seems quite stable at room temperature and will last several weeks in a well-sealed container.

(3) K. Freudenberg and F. Brauns, *Chem. Ber.*, **55**, 3233 (1922).

(4) G. W. Kenner and M. A. Murray, *J. Chem. Soc.*, S178 (1949).

(5) D. B. Denney and B. Goldstein, *J. Org. Chem.*, **21**, 479 (1956).

(6) For example, sodium-liquid ammonia cleavage of *exo*-bicyclo[3.2.1]octan-8-yl toluenesulfonate was found to yield both *exo*- and *endo*-bicyclo[3.2.1]octan-8-ol, whereas sodium naphthalene cleavage gives exclusively the *exo* alcohol.

(7) J. Kovacs and U. R. Ghatak, *J. Org. Chem.*, **31**, 119 (1966).

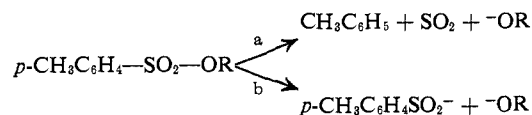
Table I. Cleavage of Toluenesulfonates with Sodium Naphthalene^a

Toluenesulfonate ^b	Sodium naphthalene, %	Yield of alcohol, ^c %
Cyclohexyl ^d	2–6	100
Cyclopentyl	6	98
<i>cis</i> -4-Cyclooctenyl ^e	3	98
Menthyl	6	98
<i>trans</i> -2-Phenylcyclohexyl ^f	6	93 ^g
Cholesteryl	6	95 ^h
Phenyl	6	99
Stearyl	6	99
Neopentyl	5	85
2-Phenylethyl	6	99
2-(1-Naphthyl)ethyl	6	98
2-Octyl	6	99
<i>exo-cis</i> -Bicyclo[3.3.0]octan-2-yl	6	100 ^h
<i>exo</i> -Norbonyl ^e	6	95 ⁱ
2,2-Dimethyldioxolan-4-methyl	6	98
Phenylcyclopentylcarbinyl	6	60 ^j

^a Unless otherwise indicated, reactions were carried out by injecting a concentrated tetrahydrofuran solution of the toluenesulfonate into about 10 ml of 0.3 *M* sodium naphthalene at 25° .

^b All toluenesulfonates had melting points identical with literature values, or yielded within 2% of the theoretical amount of acid on solvolysis. ^c Determined by gas chromatography. Listed values have an error of about $\pm 2\%$. ^d The corresponding benzenesulfonate and bromobenzenesulfonate also yielded the theoretical amount of cyclohexanol. ^e Reaction was carried out at -80° . ^f This ester was insoluble in tetrahydrofuran and was added as a solid. True yield is probably higher since it was clear some was lost on introduction. ^g Cholesterol was isolated by chromatography on alumina; the melting point was 2° below that of pure cholesterol. Thin layer chromatography showed some impurities, but one recrystallization yielded pure cholesterol. ^h Use of a very small sample introduced a larger error ($\pm 10\%$) into determination of the yield. ⁱ After a 1-min reaction time at -80° a 70% yield of *exo*-norborneol was obtained. Allowing 10 min at -80° before quenching with water gave a yield of 95%. ^j About 20% of olefin was also produced from this very reactive toluenesulfonate.

A tentative reaction scheme, similar to that of Kovacs and Ghatak,⁷ is shown. Both paths lead to alkoxide, but path a predominates at high anion radical



concentrations and leads to toluene and SO_2 which is probably converted to $\text{S}_2\text{O}_4^{2-}$ under these conditions. A more detailed description of the mechanism must await further work.

Other arene anion radicals may be used. Sodium phenanthrene appears to work almost as well; sodium anthracene reacts much more slowly and gives decidedly poorer yields (*ca.* 50% with cyclohexyl toluenesulfonate). Sodium benzophenone ketyl in tetrahydrofuran apparently does not act as a reducing agent at all for sulfonates even though the reduction potential of benzophenone ($-e^{1/2} = 1.22 \text{ v}$)⁸ is comparable to that of anthracene ($-e^{1/2} = 1.46 \text{ v}$).⁹ Cyclohexyl toluenesulfonate yields only cyclohexene on treatment with the ketyl in a quite slow reaction. (Analogously, sodium anthracene is 10^3 times more reactive in the reduction of organic halides than sodium benzophenone.¹⁰)

(8) C. A. Streuli and W. D. Cooke, *Anal. Chem.*, **26**, 963 (1954).

(9) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).

(10) H. V. Carter, B. J. McClelland, and E. Warhurst, *ibid.*, **56**, 343 (1960).

Several experiments indicate that benzenesulfonates and bromobenzenesulfonates are also readily cleaved to alkoxides by sodium naphthalene, but that a competing reaction, reduction of the alkyl group to alkane, becomes important in the case of methanesulfonates. Similar results have been reported by Cram and Dalton for the reaction of methanesulfonates with potassium in ether solvents.¹¹ In related studies preliminary experiments indicate sodium naphthalene to be an excellent agent for the reductive cleavage of toluenesulfonamides. This, and more detailed discussions of the mechanism and scope of the toluenesulfonate cleavage reaction, will be dealt with in future articles.

(11) D. J. Cram and C. K. Dalton, *J. Am. Chem. Soc.*, **85**, 1268 (1963).

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Ion-Molecule Reactions in the Liquid and Solid Phase Radiolysis of Hydrocarbon Mixtures¹

Sir:

The spectrophotometric observations of cations and anions by Hamill and co-workers² have conclusively demonstrated that, in hydrocarbon glasses, cations may take part in ion-molecule reactions prior to recombination with a negatively charged species. Furthermore, Freeman and Fayadh³ have noted that, in the liquid phase, most ion pairs undergo recombination in a period of $10^{-10 \pm 1}$ sec, and therefore they concluded that there may be sufficient time for ionic processes to occur.

Although it is thus well established that fast ion-molecule reactions can occur in both liquid and solid phase radiolysis of hydrocarbons, it has not until now been possible to unambiguously identify a particular stable product formed in the radiolysis of pure hydrocarbons or hydrocarbon mixtures as originating from a well-defined ion-molecule reaction. The occurrence of proton-transfer reactions involving the parent ion has occasionally been suggested, but the importance of such a reaction is difficult to establish, because the resulting products are usually not clearly distinguishable from those produced by free-radical reactions involving thermal or hot H atoms.

In recent years, progress has been made toward a better understanding of ion-molecule reactions occurring in the gas-phase radiolysis of hydrocarbons.⁴ It was, therefore, considered timely to initiate similar systematic investigations of ion-molecule reactions occurring in

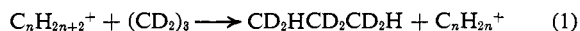
(1) This research was supported by the U. S. Atomic Energy Commission.

(2) See, for instance, (a) P. S. Rao, J. R. Nash, J. P. Guarino, M. R. Ronayne, and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 500 (1962); (b) M. R. Ronayne, J. P. Guarino, and W. H. Hamill, *ibid.*, **84**, 4230 (1962); (c) J. P. Guarino and W. H. Hamill, *ibid.*, **86**, 777 (1964).

(3) G. R. Freeman and J. M. Fayadh, *J. Chem. Phys.*, **43**, 86 (1965).

(4) (a) I. B. Sandoval and P. J. Ausloos, *ibid.*, **38**, 2454 (1963); (b) R. P. Borkowski and P. Ausloos, *ibid.*, **40**, 1128 (1964); (c) P. Ausloos and S. G. Lias, *ibid.*, **40**, 3599 (1964); (d) *ibid.*, **43**, 127 (1965); (e) *Discussions Faraday Soc.*, No. 39, 36 (1965).

the liquid and solid phase radiolysis. Because in the condensed phase fragmentation of the parent ion will occur to a much lesser extent than in the gas phase,⁵ the parent ion will play a major role in the ionic reaction mechanism. In the gas phase radiolysis^{4d} and photoionization⁶ of alkanes, exothermic H₂-transfer reactions from the parent ion to cyclopropane or to a lower olefin such as propylene have been shown to



occur even when these additives constitute only 1% of the total reaction mixture. If the distinctive propane products formed in these reactions are observed in the liquid and solid phase radiolysis of these systems, then their presence would constitute unambiguous proof that the parent ion can indeed undergo ion-molecule reactions in the condensed phase. In addition, variations in the yield of this product would provide information about the number of parent ions which could undergo reaction in competition with other processes such as neutralization under various experimental conditions. The following rather striking experimental observations show that ion-molecule reactions involving the parent ion indeed occur with high efficiency in the liquid and solid phase radiolysis.

1. Addition of 5 mole % of cyclo-C₃D₆ to perprotonated *n*-pentane, isopentane, *n*-hexane, or 3-methylpentane results in the formation of CD₂HCD₂CD₂H as a major product [*G* (molecules per 100 ev) = 0.5–1.0] with the exclusion of any significant amount of other deuterated propanes. *G*(CD₂HCD₂CD₂H) does not vary by more than 20% when the temperature is varied from 77 to 300°K. An increase in the concentration of cyclo-C₃D₆ from 1 to 10 mole % raises *G*(CD₂HCD₂CD₂H) by 50% at most. On the other hand, addition of 1 mole % of CCl₄ increases the value of *G*(CD₂HCD₂CD₂H) to 2.5, both at 77 and 193°K. The latter value is independent of the concentration of cyclo-C₃D₆. This result is consistent with the spectrophotometric observations of Guarino and Hamill,^{2c} which demonstrate that CCl₄ is an excellent electron trap whose addition to a hydrocarbon should increase the chances that the parent ion will react prior to neutralization.

2. In order to determine if, in the experiments mentioned above, CD₂HCD₂CD₂H is indeed formed by an H₂-transfer reaction rather than by two consecutive H-atom transfer processes, 1 mole % of cyclo-C₃D₆ was added to an equimolar *i*-C₅H₁₂-*i*-C₅D₁₂ mixture containing 1 mole % CCl₄. Mass spectrometric analysis of the propane which was formed with a *G* value of 2.2 was as follows: CD₃CD₂CD₃, 40%; CD₃CD₂CD₂H, 5%; CD₂HCD₂CD₂H, 50%; (C₃D₃H₃ + C₃D₄H₄ + C₃D₃H₅ + C₃D₂H₆), <1%; (C₃D₁H₇ + C₃H₈), ~5%. The observed propane composition clearly demonstrates that the large majority of the propane is indeed formed by a one-step reaction involving the transfer of a hydrogen molecule to cyclopropane. Similar isotopic analyses were obtained when equimolar *n*-C₄H₁₀-*n*-C₄D₁₀ mixtures, or *n*-C₅H₁₂-*n*-C₅D₁₂ mixtures, were irradiated in the presence of cyclo-C₃D₆.

(5) (a) P. Ausloos and S. G. Lias, *ibid.*, No. 36, 66 (1963); (b) A. Scala, S. G. Lias, and P. Ausloos, to be published.

(6) (a) R. D. Doepker, and P. Ausloos, *J. Chem. Phys.*, **42**, 3746 (1965); (b) P. Ausloos and S. G. Lias, to be published.