The mixture was subjected to PTLC on two EM plates developed with 5% methanol–ethyl acetate. The band containing **6** was removed and again subjected to PTLC on four EM plates developed with 8% methanol–chloroform. Elution of the band corresponding to **2** afforded 12 mg of recovered **2**. The product band was removed and crystallized from acetone–benzene yielding 31 mg of **6** (41.9% based on recovered **2**). Recrystallization from acetone–carbon tetrachloride afforded a pure sample of **6**: mp 133.5–136.5 °C; $[\alpha]^{26}{}_D$ −133.7° (*c* 0.155, MeOH); UV (MeOH) λ_{max} (ϵ) 280 (1550), 270 (2600), 253 (5350), 223 (16,220) nm; IR (KBr) 2.97, 5.84, 6.95, 7.01, 7.68, 7.88, 8.99, 9.20, 9.38, 9.90, 10.3, 10.7, 11.5, 12.0, 13.4, 13.7, 14.3, 14.6 μm; NMR ($CDCl_3$) δ 1.60 (3 H, s, OH), 2.86 (1 H, br s, 4-H), 3.35 (1 H, d, J = 4 Hz, 5-H), 3.57 (1 H, s, 6-H), 3.65 (1 H, m, 3-H), 3.91 (1 H, d, J = 8.5 Hz, 2-H), 4.16, 4.87 (2 H, 2d, J = 12 Hz, 7-H), 7.26–8.07 (10 H, m, aromatic protons); mass spectrum M^+ at *m/e* 388.0985 (Calcd for $C_{20}H_{20}O_6S$: 388.0980), 357, 299, 284, 248, 230, 218, 217, 195, 178, 177, 165, 163, 152, 139, 135, 123, 122, 111, 110, 109, 106, 105, 77.

Hydrolysis of 4 or 5. The hydrolysis reaction of either **4** or **5** leads to the same product **6**. For simplicity, the description of the hydrolysis of **4** is given. To a 5-mL chloroform solution containing 27 mg of **4** was added 1 mL of a solution of triethylamine–water–methanol (1:1:8). The solution was allowed to stand for 5 min, the solvent was removed in vacuo, and the residue was subjected to PTLC on two EM plates developed with 8% methanol–chloroform. The band corresponding to **6** was removed and crystallized from acetone–hexanes to afford 15 mg of **6** (68.2%) which was identical by mixture TLC, mixture melting point, IR, and NMR with an authentic sample of **6**.

Anal. Calcd for $C_{20}H_{20}O_6S \cdot {}^1\!/_2H_2O$: C, 60.44; H, 5.32; S, 8.07. Found: C, 60.68; H, 5.10; S, 8.04.

Acknowledgments. We wish to thank Dr. Gary A. Howie of the University of Virginia for helpful discussions.

Registry No.—**1**, 20421-13-0; **2**, 64011-11-6; **3**, 20421-15-2; **4**, 64011-12-7; **5**, 64011-13-8; **6**, 64011-14-9; thiophenol, 108-98-5.

References and Notes

(1) (a) Tumor Inhibitors 127. For previous paper in the series, see S. M. Kupchan, K. L. Stevens, E. A. Rohlfing, B. R. Sickles, A. T. Sneden, R. W. Miller, and R. F. Bryan, *J. Org. Chem.*, submitted for publication. (b) This work was supported by grants from the National Cancer Institute (CA-11718) and the American Cancer Society (CH-42L) and a Postdoctoral Fellowship grant to W.L.S. from the National Cancer Institute, National Institutes of Health (CA-02888-02). (c) Deceased Oct 19, 1976.

(2) S. M. Kupchan, R. J. Hemingway, and R. M. Smith, *J. Org. Chem.*, **34**, 3898 (1969).

(3) S. M. Kupchan, *Fed. Proc.*, **33**, 2288 (1974), and references therein.

(4) R. L. Hanson, H. A. Lardy, and S. M. Kupchan, *Science*, **168**, 378 (1970).

(5) S. Remillard, L. I. Rebhun, G. A. Howie, and S. M. Kupchan, *Science*, **189**, 1002 (1975).

(6) S. M. Kupchan, S. P. Ericksen, and M. Friedman, *J. Am. Chem. Soc.*, **88**, 343 (1966); S. M. Kupchan, S. P. Ericksen, and Y.-T. S. Liang, *J. Am. Chem. Soc.*, **88**, 347 (1966).

(7) The structures of **4**, **5**, and **6** were assigned based on comparisons of the NMR signals of the C-4 and C-5 protons in each compound with the NMR data for the known monochlorohydrin and monoiodohydrin of crotepoxide given in ref 2.

(8) No product corresponding to addition at C-4 was obtained. As noted by a referee, it is possible that thiol addition occurs at both C-4 and C-5 and that rapid rearrangement then occurs to afford exclusively the C-5 addition product (**6**).

(9) S. M. Kupchan and R. M. Schubert, *Science*, **185**, 791 (1974).

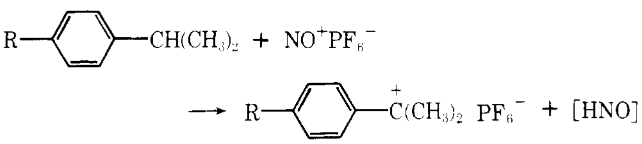
Preparative Carbocation Chemistry. 13.[1] Preparation of Carbocations from Hydrocarbons via Hydrogen Abstraction with Nitrosonium Hexafluorophosphate and Sodium Nitrite–Trifluoromethanesulfonic Acid

George A. Olah,* George Salem, John S. Staral,
and Tse-Lok Ho

*Department of Chemistry, University of Southern California,
Los Angeles, California 90007, and the Department of
Chemistry, Case Western Reserve University,
Cleveland, Ohio 44101*

Received April 25, 1977

In 1966, we reported the observation that nitrosonium salts are capable of initiating the condensation reaction of cumene (cymene),[2] indicating that abstraction of a benzylic hydrogen occurs to generate the cumyl (cymyl) cation as an intermediate. The necessity of the presence of an activated, abstractable benzylic hydrogen was demonstrated in the observation that neither toluene nor *tert*-butylbenzene reacts with $NO^+PF_6^-$ under similar conditions.[2] Ring nitrosation of the alkylbenzenes was not observed. This is in accord with previous observations[3] that electrophilic aromatic nitrosation is successful only with highly activated systems such as phenol and *N,N*-dimethylaniline.



Various reactions involving NO^+ as a hydrogen-abstracting agent in the gas phase have been subsequently reported. Searles and Sieck[4] observed the reaction of normal, branched, and cyclic alkanes having three to six skeletal carbons with NO^+. Hunt and Ryan also noted that the nitrosonium ion can act as a hydrogen abstractor (or electrophile)[5] toward various organic substrates in the ion source of a mass spectrometer. Williamson and Beauchamp[6] studied the reaction of NO^+ with such simple organic molecules as acetaldehyde and isobutane by ion cyclotron resonance spectroscopy.

More recently, we have found that nitrosonium salts can also be used advantageously in synthetic reactions. Benzyl alcohols are oxidized to arylcarbonyl products and aliphatic or alicyclic secondary alcohols are converted into ketones in good yields via reaction of their trimethylsilyl or tributylstannyl derivatives with nitrosonium tetrafluoroborate.[7] Benzyl and benzhydryl esters are oxidatively cleaved to the parent carboxylic acids and benzaldehyde or benzophenone, respectively.[8] This latter reaction represents a mild procedure to deblock esters to the corresponding acids which is complementary to the existing reductive methods.[9] All these reactions include hydrogen abstraction as the initial step.

In continuation of our study of carbocation chemistry and broadening the scope of reactions initiated by nitrosonium and nitronium salts, we now wish to describe the preparation of stable carbocations by hydrogen abstraction from their hydrocarbon precursors with nitrosonium salts.

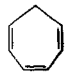
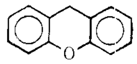
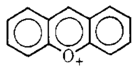
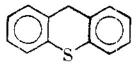
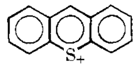
Results and Discussion

Representative hydrocarbons capable of forming stable carbocations upon hydrogen abstraction were reacted with nitrosonium hexafluorophosphate.

$$RH + NO^+PF_6^- \rightarrow R^+PF_6^- + [HNO]$$

The expected ions were cleanly formed. Nitrosonium hexafluorophosphate was used in the reactions because of its higher solubility in most of the suitable solvents than, for example, of the tetrafluoroborate salt. The reactions were carried out under a variety of conditions. Solvents used were sulfur dioxide, sulfuryl chlorofluoride, acetonitrile, and trifluoromethanesulfonic acid. Reaction of the precursor hydrocarbons with these solvents was not detectable by NMR spectroscopy within the durations normally required for their complete reaction with $NO^+PF_6^-$, although Nojima and Tokura[10] described the formation of cation radicals from electron-rich molecules in liquid sulfur dioxide. Kantner and Kreevoy[11] have, moreover, reported the disproportionation of the triphenylmethane in triflic acid. However, control experiments have indicated that such side reactions do not occur under our milder conditions, i.e., 0 °C, as neither the tri-

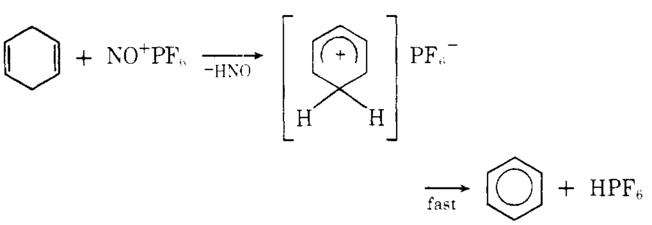
Table I. Hydrogen Abstraction from Hydrocarbons by Nitrosonium Ion

Hydrocarbon	Registry no.	Carbocation	Registry no.	% conversion[d] $NO^+PF_6^-$	% conversion[d] $NaNO_2$ + CF_3SO_3H
Ph_3CH	519-73-3	Ph_3C^+	13948-08-8	~100[a] ~100[b]	~100[a]
	544-25-2		26811-28-9	~100[a]	~100[a]
Ph_2CHCH_3	1612-00-0	$Ph_2C^+CH_3$	16805-85-9	88[c]	
Ph_2CH_2	101-85-5	Ph_2CH^+	709-82-0	71[c]	
$PhCH(CH_3)_2$	78-82-8	$PhC^+(CH_3)_2$	16804-70-9	83[c]	
	92-83-1		261-23-4	~100[a]	~100[a]
	261-31-4		261-32-5	~100[a]	~100[a]

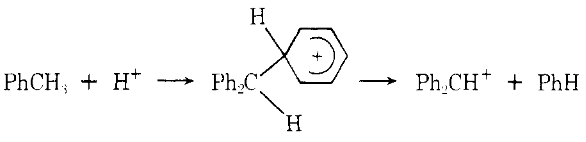
[a] Based on ^1H NMR analysis of formed carbocation. [b] Yield of product isolated after recrystallization from CH_2Cl_2. [c] Based on GLC analysis of corresponding alcohol obtained after quenching the carbocation solution with H_2 (see Experimental Section). [d] Registry no.: $NO^+PF_6^-$, 16921-91-8; $NaNO_2$, 7632-00-0; CF_3SO_3H, 1493-13-6.

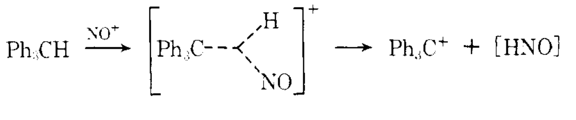
phenylmethyl nor diphenylmethyl cation was observed (by NMR) in these solutions. The products were identical to those previously reported.[12] Quenching with water or methanol yielded the expected alcohols or methyl ethers, respectively. These results are summarized in Table I.

When 1,4-cyclohexadiene is reacted with $NO^+PF_6^-$ in SO_2ClF at −78 °C,[13] the quantitative formation of benzene is observed. This observation, in view of the known instability of the parent benzenium ion, suggests the pathway shown below. This ionization–deprotonation route is reminiscent of the cumene-α-methylstyrene transformation[2] and the dehydrogenation of 9,10-dihydroanthracene.[14]



The formation of the triphenylmethyl cation from the reaction of triphenylmethane with nitrosonium ion is of particular interest. The related ionization of triphenylmethane with superacids leads to protolysis via C–C bond cleavage giving benzene and the diphenylmethyl cation.[11,15] In this case, the reaction most probably takes place by way of protonation of the aromatic ring, with the proton eventually shifting to the ipso carbon, followed by cleavage of the diphenylmethyl cation. On the other hand, electrophilic aromatic nitration occurs exclusively when triphenylmethane is reacted with nitronium salts.[16] The reversible nature of aromatic ring nitrosation, however, seems to allow the NO^+ ion to migrate toward the exocyclic carbon and to insert into the tertiary C–H bond to form the two-electron three-center-bonded carbonium ion which subsequently cleaves to the triphenylmethyl cation.





The evolution of brown fumes of nitrogen dioxide has been repeatedly observed during reactions which were exposed to air. This implies that nitric oxide was formed and oxidized. Since the carbocation products are derived from their precursor hydrocarbons via hydrogen abstraction by NO^+, the required cleavage product is HNO. Harteck[17] has shown that HNO readily dimerizes to dihydroxydiazene, which decomposes into water and nitrous oxide. In order to demonstrate that hydrogen is indeed removed by NO^+ in the reactions to generate HNO, the gaseous product(s) of an anaerobic reaction was collected and analyzed by GC–MS. An identical GC retention time with that of an authentic sample, in addition to a strong m/e 44 peak in the mass spectrum, conclusively established N_2O as the major gaseous product.

$$2HNO \rightleftharpoons HON{=}NOH \rightarrow H_2O + N_2O$$

Having found a suitable new way to generate stable carbocations from hydrocarbons with nitrosonium salts, we further studied the simplification of this method by an in situ generation of NO^+. Nitrosonium triflate is readily produced according to the following equation:

$$3CF_3SO_3H + NaNO_2 \rightarrow NO^+CF_3SO_3^- + H_3O^+CF_3SO_3^-$$

The $NaNO_2$–CF_3SO_3H system was found to be particularly efficient in effecting hydrogen abstraction from hydrocarbons. Facile, quantitative reaction took place with the corresponding hydrogen donors, as exemplified by the rapid generation of the triphenylmethyl, cycloheptatrienyl, xanthyl, and thioxanthyl cations.

In conclusion, we have developed a novel procedure for preparing stable carbocations from hydrocarbons via hydrogen abstraction by nitrosonium salts. In our opinion, this method is superior to that employing the triphenylmethyl cation as the hydrogen-abstracting agent, because (1) the nitrosonium ion is more effective and of more general utility as demonstrated, for example, in its ability to generate the triphenylmethyl cation from triphenylmethane, and (2) no organic by-products are formed, a distinct advantage in terms of preparative and spectroscopic convenience. The preparation of carbocations from hydrocarbons via hydrogen abstraction with either NO^+ or $(C_6H_5)_3C^+$ salts is, however, by necessity limited to systems which give sufficiently stabilized carbocationic products.

Experimental Section

All hydrocarbon precursors used were either commercially available or synthesized by known procedures. Nitrosonium hexafluorophosphate (Cationics, Inc.) and trifluoromethanesulfonic acid (3M Company) were used without further purification.

The ^{1}H NMR spectra were recorded on a Varian Associates A56/60A spectrometer and the ^{13}C NMR spectra were obtained on a Varian Associates XL-100 spectrometer operating in a pulsed FT mode. Chemical shifts were measured from an external (capillary) Me_4Si signal. Gas chromatographic analyses of the quenched products were obtained on a Hewlett-Packard 5700A gas chromatograph with a 2 ft × 1/8 in. SE-30 column eluted with helium at 250 °C.[18a] GC-MS were obtained on a DuPont 21-094 mass spectrometer coupled to a Varian Associates Aerograph 2700 gas chromatograph using a 10 ft × 1/8 in. Porapak Q column eluted with helium.

Hydrogen Abstraction from Hydrocarbons with Nitrosonium Hexafluorophosphate. To a solution of $NO^+PF_6^-$ (1.40 g, 8 mmol) in ca. 5 mL of liquid sulfur dioxide at −78 °C was slowly added an appropriate hydrocarbon (4 mmol). The reaction vessel was sealed and kept at room temperature for 3 h. Thereafter the solution was cooled to −20 °C, the vessel was opened, and aliquots were analyzed, upon transfer to NMR tubes by spectral analysis and, after hydrolysis, by GLC by comparison with known amounts of standard pure alcohols.

Triphenylmethyl (mp ~146 °C dec)[18b] and cycloheptatrienyl hexafluorophosphate (mp 210–215 °C dec) were isolated in quantitative yield upon recrystallization of the residue, obtained from the evaporation of the volatile components of the reaction mixture, from CH_2Cl_2.

Hydrogen Abstraction from Hydrocarbons by Nascent Nitrosonium Ion. To ice-cooled trifluoromethanesulfonic acid (6.75 g, 45 mmol) was added sodium nitrite (1.05 g, 15 mmol), followed by the hydrocarbon precursor (5 mmol) while the mixture was stirred with a Fisher Vortex stirrer. After 10 min, an aliquot was taken to record the NMR spectra. Complete consumption of the starting material was observed and the spectra observed were those of the carbocationic species.

Acknowledgment. Support of our work by the National Institutes of Health and the National Science Foundation is gratefully acknowledged.

Registry No.—Cycloheptatrienyl hexafluorophosphate, 29663-54-5; nitrosonium triflate, 51637-52-6.

References and Notes

(1) Part 12. G. A. Olah and T.-L. Ho, *Synthesis*, 798 (1976).
(2) G. A. Olah and N. Friedman, *J. Am. Chem. Soc.*, **88,** 5330 (1966).
(3) Z. J. Allan, J. Podstata, D. Snobl, and J. Jarkovsky, *Tetrahedron Lett.*, 3565 (1965).
(4) S. K. Searles and L. W. Sieck, *J. Chem. Phys.*, **53,** 794 (1970).
(5) D. F. Hunt and J. F. Ryan, *J. Chem. Soc., Chem. Commun.*, 620 (1972).
(6) A. D. Williamson and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97,** 5714 (1975).
(7) G. A. Olah and T.-L. Ho, *Synthesis*, 609 (1976).
(8) T.-L. Ho and G. A. Olah, *Synthesis* (in press).
(9) J. W. F. McOmie, Ed., "Protective Groups in Organic Chemistry", Plenum Press, London and New York, 1973.
(10) T. Ando, M. Nojima, and N. Tokura, *J. Chem. Soc., Chem. Commun.*, 989 (1975); M. Nojima, G. Nagao, N. Kakeya, M. Takagi, and N. Tokura, *ibid.*, 486 (1976).
(11) S. S. Kantner and M. M. Kreevoy, *J. Org. Chem.*, **42,** 865 (1977).
(12) (a) G. A. Olah and P. Westerman, *J. Am. Chem. Soc.*, **95,** 7530 (1973); (b) T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32,** 1558 (1967); (c) P. M. Bower, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc. B*, 1511 (1971); (d) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).
(13) Experiments were carried out by Dr. G. Asensio.
(14) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).
(15) (a) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Am. Chem. Soc.*, **94,** 2038 (1972); (b) M. Kreevoy, personal communication, on similar cleavage with trifluoromethanesulfonic acid.
(16) G. A. Olah and H. C. Lin, unpublished results.
(17) P. Harteck, *Ber.*, **66,** 423 (1933).
(18) (a) The yields and purities of the products in these reactions were conveniently determined upon comparison of the GC areas of the products obtained with those produced by standardized amounts of the compounds under identical instrument conditions; (b) G. A. Olah, J. J. Svoboda, and J. A. Olah, *Synthesis*, 544 (1972).
(19) J. J. K. Boulton and L. P. Ellinger, British Patent 1 134 736 (1968); *Chem. Abstr.*, **70,** 29545n (1969).

Carbon Monoxide–Hydrogen–Water: Reduction of Benzophenone, Diphenylcarbinol, and Diphenylmethane

D. Jones, R. J. Baltisberger, K. J. Klabunde, N. F. Woolsey,
and V. I. Stenberg*

*Department of Chemistry, University of North Dakota,
Grand Forks, North Dakota 58202*

Received May 17, 1977

Introduction

A mixture of carbon monoxide and water is regarded to be superior to hydrogen as a reducing agent for the liquefaction of lignite.[1–5] How carbon monoxide functions in the lignite reduction is still largely a matter of speculation. Since a mixture of carbon monoxide and hydrogen can be made from lignite and its inherent water by the water gas reaction, the commercial utilization of carbon monoxide or a mixture of carbon monoxide and hydrogen as a reducing agent is promising. Sodium carbonate, ferrous sulfide, and the mineral matter in lignite are reported to be catalysts for liquefaction. Appell et al.[4] have proposed that sodium carbonate reacts with the water to form a basic medium, and the base interacts with carbon monoxide to give the formate ion. The formate ion is a reducing agent which augments the reducing power of the hydrogen present, particularly for carbonyl compounds. Appell et al.[4] has suggested that hydrogen more so than carbon monoxide favors the cracking of carbon chains.[4]

A study of the carbon monoxide reduction mechanism is of direct value for developing improved catalysts for the liquefaction process, as well as for reduction of other organic compounds. This study relates data on the reduction of model compounds which best represent critical chemical linkages in lignite. The three title compounds contain one-carbon linkages between aromatic rings. A comparison has been made with hydrogen, hydrogen–carbon monoxide–water, and carbon monoxide–water as reducing gases, sodium carbonate, sodium formate, sodium hydroxide, and iron oxide as possible catalysts, and tetralin as a hydrogen donor solvent.

Results and Discussion

The reduction products of benzophenone are diphenylcarbinol, diphenylmethane, benzene, and toluene. Diphenylcarbinol, under the same conditions, gives diphenylmethane, benzophenone, benzene, and toluene. Diphenylmethane is only converted in low yield, i.e., 1–3%, to benzene and toluene by even the most rigorous of conditions.

The order of conversion effectiveness of the reducing gases in the presence of sodium carbonate for the benzophenone reduction is hydrogen < carbon monoxide–water < carbon monoxide-water-hydrogen (Table I). For diphenylcarbinol, the order is hydrogen < carbon monoxide–water ≃ carbon monoxide-water-hydrogen (Table II). The hydrogen donor solvent tetralin has no influence on the conversion yields for the carbon monoxide-water-hydrogen reduction (runs 6 and 9, Table I), the carbon monoxide–water reduction (runs 2 and 8, Table I), and the hydrogen reduction (runs 5 and 10, Table I). However, tetralin did influence the product distribution by causing more diphenylmethane to be formed at the expense of diphenycarbinol (runs 2 vs. 8 and 5 vs. 10, Table I), though this is not consistent (run 6 vs. 9, Table I).

The reduction of diphenylcarbinol gives disproportionation in addition to reduction. Diphenylcarbinol, in the absence of reducing gases under the reaction conditions, gives a 1:1 molar ratio of benzophenone to diphenylmethane, cf. run 1, Table II. Sodium carbonate is not necessary for the disproportionation, cf. runs 1 and 2, Table II.