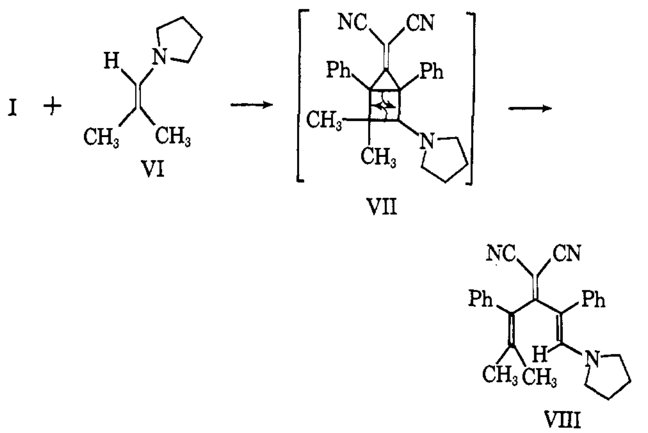
cps), 3.11 (4 H, quartet, $J = 7$ cps), 4.97 (H_B, triplet, $J_{AB} = J_{BC} = 12$ cps), 5.43 (H_D or H_E, singlet, $J_{DE} = 0$), 6.00 (H_E or H_D, singlet, $J_{ED} = 0$), 6.76 (H_C, doublet, $J_{CB} = 12$ cps), 7.13–7.60 (11 H, complex multiplet, aromatics and H_A).[5] *Anal.* Calcd for $C_{26}H_{25}N_3$: C, 82.29; H, 6.64; N, 11.07; mol wt, 379. Found: C, 82.41; H, 6.87; N, 11.04; (mass spectrum) *m/e* 379.

Tetraene IV[6] must arise from an initial 1,2 cycloaddition of the 3,4-double bond of II[7] to the endocyclic double bond of I[8] and subsequent ring opening of the bicyclic intermediate III.[9]

Reaction of 0.723 mmole of 1-(N-pyrrolidino)-2-methylpropene (VI) with 0.618 mmole of I in benzene under similar conditions produced triene VIII as yellow plates in 92% yield after similar work-up and recrystallization from benzene–hexane: mp 188–189°; $\nu_{max}^{CHCl_3}$ (cm^{-1}) 2210 (s), 1585 (s), 1455 (s), 1390 (s), 1310 (s); $\lambda_{max}^{C_2H_5OH}$ (mμ) 403 (ϵ 43,300), 236 (15,200), 290 (sh) (3600); nmr (CDCl$_3$) (ppm from TMS) 1.5–1.8 (4 H, $-CH_2CH_2-$, multiplet), 1.88 (3 H, CH_3-, singlet), 1.98 (3 H, CH_3-, singlet), 2.7–3.3 (4 H, $-CH_2NCH_2-$, broad singlet), 7.05–7.40 (10 H, multiplet, aromatics), 7.56 (vinyl H, singlet). *Anal.* Calcd for $C_{26}H_{25}N_3$: C, 82.29; H, 6.64; N, 11.07; mol wt, 379. Found: C, 82.29; H, 6.86; N, 11.09; (mass spectrum) *m/e* 379.



The production of compounds IV and VIII necessitates the intermediacy of the substituted 5-methylenebicyclo[2.1.0]pentane derivatives III and VII,[10] respectively. Whether the formation as well as the ring opening of intermediates III and VII proceeds by a concerted or stepwise process is questionable.

Further investigations of these reactions employing other enamines as well as triafulvenes are in progress.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM 14579-01) for generous support of this work.

---

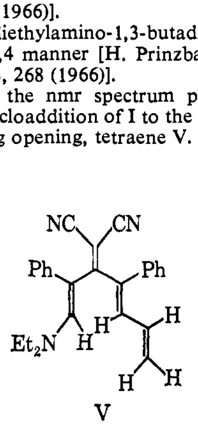
[5] The nmr spectra were recorded with a Varian A-60-A spectrometer. Mass spectral data were recorded on a Hitachi RMU-6D spectrometer. The infrared and ultraviolet data were taken on a Perkin-Elmer Model 337 grating spectrophotometer and a Cary Model 14 spectrophotometer, respectively. The A-60-A and RMU-6D spectrometers were purchased through a National Science Foundation major equipment grant to Brown University.

[6] Examination of Dreiding models reveals that the tetraene probably possesses the more favorable *trans,trans* geometry.

[7] The cycloaddition of sulfene ($CH_2{=}SO_2$) proceeds by initial attack at the 3,4-double bond of 1-dialkylamino-1,3-butadienes [G. Opitz and F. Schweinsberg, *Angew. Chem.*, 77, 811 (1965); Leo A. Paquette, private communication]. Ketene, on the other hand, undergoes cycloaddition to the 1,2-double bond of 1-(2-ethyl-4-methyl-1,3-pentadien-1-yl)piperidine [R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, 31, 1931 (1966)].

[8] The addition of 1-diethylamino-1,3-butadiene to a dibenzocalicene derivative proceeds in 1,4 manner [H. Prinzbach, U. Fischer, and R. Cruse, *Angew. Chem.*, 78, 268 (1966)].

[9] The simplicity of the nmr spectrum precludes the alternative possibility of an initial cycloaddition of I to the 1,2-double bond of II to give ultimately, after ring opening, tetraene V.



V

[10] The reaction of 1,2-diphenyl-3-carbethoxymethylenecyclopropene with tetracyanoethylene reportedly proceeds across the exocyclic double bond of the triafulvene to give a spirohexene derivative [M. A. Battiste, *J. Am. Chem. Soc.*, **86**, 942 (1964)]. On the other hand, 1,2-di-*n*-propyl-3-dicyanomethylenecyclopropene fails to react with tetracyanoethylene under similar conditions [A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964)].

Joseph Ciabattoni, Edward C. Nathan, III
Metcalf Research Laboratories
Brown University, Providence, Rhode Island 02912

Received April 10, 1967

Catalysis of Hydrogen Exchange in *m*-Dinitrobenzene[1]

Sir:

In the interaction of aromatic nitro compounds with bases, nuclear hydrogen abstraction is the least well characterized process; the formation of charge-transfer complexes,[2a] of radical anions,[2b] and latterly of Meisenheimer adducts[3] is well substantiated. Due to the contradictory reports[4–10] as to the feasibility and significance of such proton abstraction we have undertaken a systematic study of the process. Further, it was hoped that these studies would also provide information on the nature of the catalysis of aromatic hydrogen abstraction. Whereas general-base catalysis of proton abstraction from aliphatic carbon (eq 1) is well documented,[11a] corresponding evidence for

---

[1] Hydrogen Exchange Studies. IV.

[2] (a) G. Briegleb, "Electronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961; (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).

[3] M. R. Crampton and V. Gold, *Chem. Commun.*, 549 (1965); R. Foster and C. A. Fyfe, *Tetrahedron*, **22**, 1831 (1966); K. L. Servis, *J. Am. Chem. Soc.*, **89**, 1508 (1967); J. H. Fendler, *et al.*, *J. Org. Chem.*, in press.

[4] J. A. A. Ketelaar, A. Bier, and H. T. Vlaar, *Rec. Trav. Chim.*, **73**, 37 (1954).

[5] V. Baliah and V. Ramakrishnan, *ibid.*, **78**, 783 (1959); **79**, 1150 (1960).

[6] R. E. Miller and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959); 4886 (1961).

[7] R. J. Pollitt and B. C. Saunders, *Proc. Chem. Soc.*, 176 (1962).

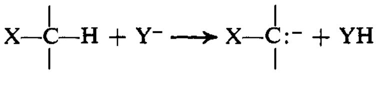
[8] R. Foster and R. K. Mackie, *Tetrahedron*, **19**, 691 (1963).

[9] M. R. Crampton and V. Gold, *J. Chem. Soc., Phys. Org.*, 498 (1966).

[10] Part III of series: E. Buncel and E. A. Symons, *Can. J. Chem.*, **44**, 771 (1966).

[11] R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959: (a) Chapters 9 and 10; (b) Chapter 4.

aromatic hydrogen has not yet been available. The reason is clearly that abstraction of aromatic hydrogen, conveniently measured by isotopic exchange, typically



$$\mathrm{X{-}\overset{|}{\underset{|}{C}}{-}H + Y^- \longrightarrow X{-}\overset{|}{\underset{|}{C}}{:}^- + YH} \qquad (1)$$

Y^- = a Brønsted base
X = $-CO-$, $-NO_2$, $-CF_3$, etc.

requires very strongly basic systems such as potassium amide in liquid ammonia[12] or lithium cyclohexylamide in cyclohexylamine;[13] these systems have afforded valuable information on relative acidities of hydrogens in different environments but have left unanswered the question whether Brønsted bases such as azide ion, amines, etc., can partake in aromatic hydrogen abstraction.

The compound chosen for study was 1,3-dinitrobenzene since this was reported[7] to exchange the 2-hydrogen under the unusually mild conditions of sodium deuterioxide in DMF–D_2O. We now report some results of the effect of a number of Brønsted bases, and also of reaction medium, on this hydrogen-exchange process. The media examined were dimethylformamide, dimethyl sulfoxide, and dimethoxyethane, containing deuterium oxide. Exchange was allowed to proceed at 30° for the more reactive bases and at 100° for the less reactive ones. The extent of exchange under standard conditions is taken to be a measure of the relative proton abstracting abilities of the bases in the particular media.

The results (Table I) indicate a dependence of reactivity on medium and base. The effect of medium is seen with reference to deuterioxide,[14] acetate, and azide ions. The DMF and DMSO media are about equally facile in base catalysis and are much more effective than DME. In considering a reactivity order with respect to base the anionic and neutral bases must be treated separately to allow for the markedly different medium effects on base strength expected for bases of different charge type;[16] the basicity of the anionic bases will be greatly enhanced by a change to a dipolar aprotic medium, but the basicity of the neutral bases will remain relatively unaffected.[16] Among the anionic bases the reactivity order, for DMF medium, is $DO^- > PhO^- > S_2O_3^{2-} \approx AcO^- > N_3^-$, which approximates a decreasing order of base strength as given by the pK_a's of the conjugate acids.[17] The data for the amines do not fall into a definite order, consistent with the known[11b,18] medium dependence of relative base strengths of primary, secondary, and tertiary amines. Pyridine is seen to be unreactive.

Table I. Exchange of the 2-Hydrogen in 1,3-Dinitrobenzene[a]

Y^- [b] (pK_a)[c]	Medium[d]	Temp, °C	% deuteration[e]
OD^- (15.7)	DMF	30	92
	DME	30	29
PhO^- (9.9)	DMF	30	42
SO_3^{2-} (7.1)	DMF	100	83
AcO^- (4.7)	DMF	100	85
	DMSO	100	86
	DME	100	0
N_3^- (4.0)	DMF	100	74
	DMSO	100	79
	DME	100	0
Piperidine (11.2)	DMF	100	45
Triethylamine (10.6)	DMF	100	24
n-Hexylamine (10.4)	DMF	100	40
1,4-Diazabicyclo-[2.2.2]octane (8.6)	DMF	100	34
Pyridine (5.4)	DMF	100	0

[a] Reaction time was 16 hr throughout. [b] The anions were present as sodium salts. Concentrations were: $[Y^-] = 0.05\ M$; [dinitrobenzene] = $0.5\ M$. In the case of the phenoxide exchange 0.05 *M* phenol was also present, to repress the deuterioxide ion concentration. [c] The pK_a values refer to water. [d] Contains 10% D_2O by volume. [e] Exchange was measured by infrared and nmr; no evidence was found for exchange of the other hydrogens of the substrate. Maximum theoretical deuteration with the experimental D:H ratio was 95%.

A number of factors are pertinent in consideration of the above results. (1) The apparent parallelism between the extent of exchange and p*K* is not alone conclusive evidence of Brønsted base catalysis, since lyate ion catalysis as the main cause of exchange is not ruled out thereby. In this respect the significantly lower reactivity of triethylamine, particularly in comparison with the unhindered tertiary amine 1,4-diazabicyclo[2.2.2]octane, which can be ascribed to steric hindrance to proton transfer,[19] argues against lyate ion catalysis as the predominant factor. (2) Evidence has been presented[20] that, as a result of hydrogen bonding, internal return in the solvated carbanions may form part of the rate-determining step in certain reaction media. In this connection it is noted that the DMF–D_2O medium was used in a similar study[21] of kinetic acidities of some carbon acids and that the derived pK_a scale was in good accord with data obtained from other studies.[22] Hence the common mechanism for these exchange processes is taken to be rate-determin-

---

(12) G. E. Hall, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, 77, 4540 (1955); A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962); J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2640 (1965).

(13) A. Streitwieser, Jr., J. R. Caldwell, R. G. Lawler, and G. R. Ziegler, *ibid.*, **87**, 5399 (1965).

(14) DMSO medium was not used in the case of deuterioxide since DMSO itself undergoes a facile deuterioxide-catalyzed hydrogen exchange.[15] No evidence was found for hydrogen exchange of DMSO in presence of azide or acetate ions.

(15) E. Buncel, E. A. Symons, and A. W. Zabel, *Chem. Commun.*, 173 (1965).

(16) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962); B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **88**, 1911 (1966); R. G. Pearson, *ibid.*, **85**, 3533 (1963); R. Gompper, *Angew. Chem. Intern. Ed. Engl.*, **3**, 560 (1964).

(17) The pK_a values quoted are for H_2O; they will be affected by a change to D_2O and also to the largely nonaqueous media. Considerations of the p*K* dependence of hydrogen exchange will be valid as long as the relative order of the p*K*'s remains unaffected by the medium changes. There is good ground for the general validity of this assumption for bases of a given charge type.[11,16] (Sulfite ion should, strictly, not be included in the series for this reason.)

(18) R. G. Pearson and D. C. Vogelsong, *J. Am. Chem. Soc.*, **80**, 1038 (1958).

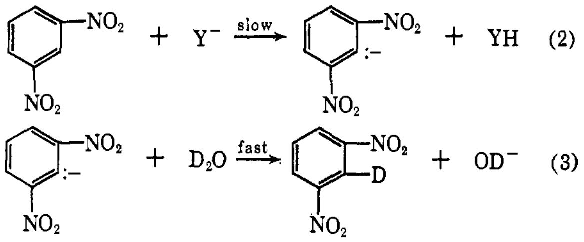
(19) V. Gold, *Progr. Stereochem.*, **3**, 169 (1962); J. A. Feather and V. Gold, *Proc. Chem. Soc.*, 306 (1963); F. Covitz and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 1773 (1963).

(20) J. E. Hofmann, A. Schriesheim, and R. E. Nickols, *Tetrahedron Letters*, 1745 (1965); W. T. Ford, E. W. Graham, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 690 (1967).

(21) R. E. Dessy, Y. Okuzumi, and A. Chen, *ibid.*, **84**, 2899 (1962).

(22) Summarized in D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 19.

ing abstraction of hydrogen by the Brønsted base, followed by fast protonation by solvent of the resulting carbanion (eq 2-4). (3) Since the reaction medium



$$\mathrm{YH} + \mathrm{OD^-} \rightleftharpoons \mathrm{Y^-} + \mathrm{HOD} \qquad (4)$$

in some of these exchange processes (Y$^-$ = OD$^-$, PhO$^-$, $S_2O_3^{2-}$) was strongly colored (deep red or purple) it is possible that the anion was partly tied up in the form of Meisenheimer adducts; on the other hand the colors may only be indicative of charge-transfer complexing. Detailed equilibrium studies with respect to complex formation, coupled with kinetic studies on the exchange process, will be required to separate these effects. The studies relevant to these factors are under active consideration.

Acknowledgment. This research was supported by a grant (PRF 1841 A-4) from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

E. Buncel, A. W. Zabel
Department of Chemistry, Queen's University,
Kingston, Ontario, Canada

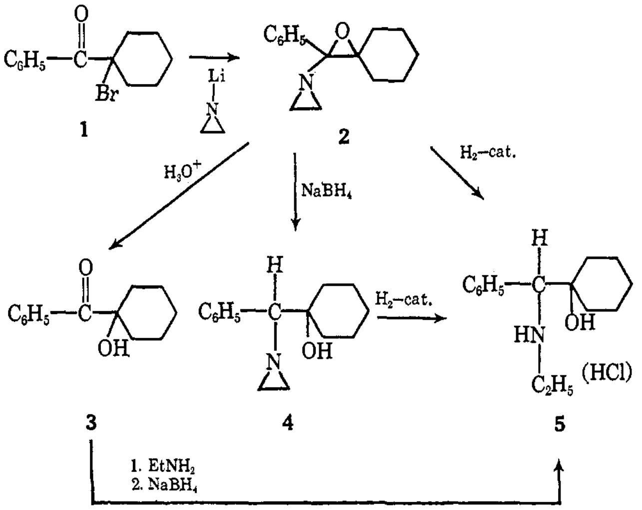
Received October 24, 1966

Epoxyamines. A New Functional Group in Organic Chemistry

Sir:

We wish to report the preparation and rearrangement of a new class of organic compounds, the epoxyamines. Although the concept of this unusual functional group has been invoked as an intermediate in several instances,[1-3] isolation and complete characterization of an example previously had not been accomplished.[4] The apparent inaccessibility of these compounds had been attributed to their high reactivity and to the possibility of facile rearrangements.[1,2]

We have now isolated a stable crystalline epoxyamine, 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.5]octane (**2**), by the action of the lithium salt of ethylenimine[5] on α-bromocyclohexyl phenyl ketone[6] (**1**) in ether at room temperature. Evaporative distillation (bath temperature 90–100° (0.01 mm)) of the crude product gave 70–75% of **2**, bp 90–95° (0.001 mm), $n^{24}\mathrm{D}$ 1.5870, which could be crystallized from pentane; mp 20–22°. The infrared spectrum was devoid of any hydroxyl and carbonyl absorptions but had strong peaks at 1025 and 1045 cm^{-1}. The nmr spectrum ($CDCl_3$) was consistent with structure **2**, showing aromatic protons from τ 2.45 to 2.85 and aliphatic protons from τ 7.8 to 9.0 in the ratio 5:14.



Hydrolysis with 2 *N* hydrochloric acid converted **2** into the known α-hydroxycyclohexyl phenyl ketone[6] (**3**) in 90% yield. Reduction of **2** with sodium borohydride in methanol gave 1-[α-(1-aziridinyl)benzyl]cyclohexanol (**4**) (60%), mp 113–114°. Hydrogenation of **4** in ethanol at atmospheric pressure using 10% palladium on carbon as catalyst yielded 1-(α-N-ethylaminobenzyl)cyclohexanol (**5**), characterized as its hydrochloride (85%), mp 223–224° dec. This amino alcohol **5** was also formed in 80% yield by direct hydrogenation of **2** in methanol using the same catalyst. The structure of **5** was confirmed by its formation from the sodium borohydride reduction of α-hydroxycyclohexyl phenyl ketone N-ethylimine, which in turn was made from ethylamine and **3** in the presence of potassium carbonate.

When heated to the reflux temperature in *o*-dichlorobenzene for 15 hr under a nitrogen atmosphere, **2** rearranged with ring expansion to give 2-(1-aziridinyl)-2-phenylcycloheptanone (**6**) in 35–38% yield, the remainder of the material being an intractable resin. This rearrangement was particularly interesting, since according to a previous postulate[7] α-(1-aziridinyl)cyclohexyl phenyl ketone (**7**) would have been the expected product. To show that **7** was not an intermediate in the transformation of **2** to **6**, **7** was prepared by the general method[8] involving the action of ethyl-

---

(1) C. L. Stevens, P. Blumbergs, and M. Munk, *J. Org. Chem.*, **28**, 331 (1963), and references cited therein.

(2) A. Kirmann and H. I. Joschek, *Bull. Soc. Chim. France*, 3483 (1963).

(3) A. Hassner and P. Catsolacos, *J. Org. Chem.*, **32**, 549 (1967).

(4) M. Mousseron, J. Jullien, and Y. Jolchine, *Bull. Soc. Chim. France*, 757 (1952), reported the formation of an epoxyamine as a by-product in the reaction of 2-chlorocyclohexanone with aqueous dimethylamine, but they did not fully characterize or establish the structure of the material.

(5) The fact that ethylenimine forms stable addition products with aldehydes and ketones suggested that it might impart stability to this class of compounds. *Cf.* A. Dornow and W. Schacht, *Chem. Ber.*, **82**, 464 (1949).

(6) C. L. Stevens and E. Farkas, *J. Am. Chem. Soc.*, **74**, 618 (1952).

(7) A. Kirmann, R. Muths, and J-J Riehl, *Bull. Soc. Chim France*, 1469 (1958).

(8) C. L. Stevens and C. H. Chang, *J. Org. Chem.*, **27**, 4392 (1962).