

of substituted cycloheptanes⁷ observed in perhydroazulenes.⁸ The application of this rearrangement to the synthesis of seven-membered aromatic compounds is now in progress.

We are indebted to Prof. F. Sondheimer for his interest and encouragement, and to Syntex S.A., Mexico, for a generous gift of starting materials, and optical rotatory dispersion measurements.

(7) H. J. E. Loewenthal and R. Rona, *J. Chem. Soc.*, 1429 (1961), and refs. cited therein.

(8) N. L. Allinger and V. B. Zalkow, *J. Am. Chem. Soc.*, **83**, 1144 (1961).

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THE WEIZMANN INSTITUTE OF SCIENCE YEHUDA MAZUR
REHOVOTH, ISRAEL MANASSE NUESIM

RECEIVED JULY 10, 1961

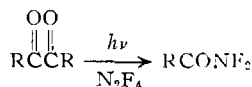
TETRAFLUOROHYDRAZINE: A VERSATILE INTERMEDIATE FOR THE SYNTHESIS OF N-FLUORO COMPOUNDS

Sir:

We have found tetrafluorohydrazine,¹ N₂F₄, to be a versatile intermediate for the synthesis of both organic and inorganic compounds containing the difluoramino group, NF₂. N₂F₄ participates in a variety of free radical reactions as might be expected from its low N-N bond strength.²

N₂F₄ and chlorine react under the influence of ultraviolet light in Pyrex to produce chlorodifluoramino,³ ClNF₂. This is an equilibrium reaction in which the formation of chlorodifluoramino is favored by a large excess of chlorine and a relatively high temperature (80°). The synthesis of difluoramino, HNF₂, by the hydrogen abstraction reaction between N₂F₄ and thiophenol has been reported.⁴

The photolysis of diketones in the presence of N₂F₄ at room temperature in Pyrex caused the formation of N,N-difluoroamides in good yield.



The reaction has been applied successfully to biacetyl, glyoxal and benzil. For example, 0.06 mole of biacetyl and 0.06 mole of N₂F₄ irradiated for sixteen hours with a Hanovia EH-4 lamp yielded 0.077 mole of N,N-difluoroacetamide (IV), b.p. 45–47°; yield 80% based on N₂F₄ consumed. *Anal.* Calcd. for C₂H₃F₂NO: N, 14.74. Found; N, 14.40. The material was characterized by its infrared spectrum ($\nu_{\text{C=O}}$ 1820 cm.⁻¹), n.m.r. spectrum⁵ (F¹⁹ resonance at -4270 c.p.s. and H¹ resonance at +190 c.p.s.), and by its solvolysis in ethanol to ethyl acetate and difluoramino.

Alkyl radicals⁶ generated by the decomposition of

(1) C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

(2) C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

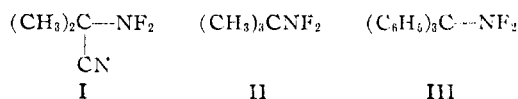
(3) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(4) J. P. Freeman, A. Kennedy and C. B. Colburn, *ibid.*, **82**, 5304 (1960).

(5) F¹⁹ resonances are recorded in cycles from external CF₃CO₂H and H¹ resonances from external C₆H₆. Negative values indicate resonance at lower field than the standard.

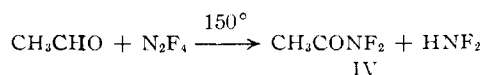
(6) The photochemical reaction between alkyl iodides and N₂F₄ presumably involves alkyl radicals; J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

azoisobutyronitrile, azoisobutane, and hexaphenyl-ethane also reacted with N₂F₄ to produce the corresponding difluoroamines, I, b.p. 71–72° (150 mm.), II, b.p. 54–55° and III, m.p. 81–82°.



Satisfactory analyses were obtained for all these compounds. Their F¹⁹ n.m.r. spectra⁵ all show signals from the NF₂ groups at -4724, -4224, and -4430 c.p.s., respectively. These compounds resist hydrolysis.

N,N-Difluoroamides also may be obtained by the reaction of aldehydes with N₂F₄. N,N-Difluoroacetamide and difluoramino were produced when acet-aldehyde and N₂F₄ were heated at 150° in a Pyrex bulb. This reaction may be compared to the conversion of benzaldehyde to benzoyl chloride by chlorine.⁷



N₂F₄ must be handled cautiously. Oxygen must be excluded rigorously from mixtures of N₂F₄ and organic compounds or explosions are likely to result. The difluoramino compounds themselves should also be handled with care.

Acknowledgment.—This work was conducted under Army Ordnance Contract DA-01-021 ORD-5135. The support and encouragement of Dr. Warren D. Niederhauser is gratefully acknowledged.

(7) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 369.

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RECEIVED JUNE 26, 1961

CARBONIUM ION SALTS. II. REACTION OF CYCLOHEPTATRIENE WITH INORGANIC HALIDES; TROPENIUM CHLOROBORATE¹

There is much interest in compounds of the chloroborate anion^{2a–1}; however, their preparation has required high temperature and pressure,^{2d} long milling of solids,^{2h} or liquid hydrogen chloride solvent,^{2g} and the products often give unsatisfactory analyses. The only easily prepared, stoichiometric chloroborate reported is cesium chloroborate.^{2i,3}

We find that the reaction of boron chloride with cycloheptatriene⁴ in methylene chloride (dry conditions under nitrogen, room temp. for 24 hr., mole ratio BCl₃/C₇H₈ of 1.4/1) gives 12.6% tropenium

(1) Supported by the Petroleum Research Fund, Grant 443-A.

(2) (a) D. R. Martin, *Chem. Rev.*, **42**, 581 (1948); (b) N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1527 (1956); (c) M. F. Lappert, *Proc. Chem. Soc.*, 121 (1957); (d) E. L. Muettterties, *J. Am. Chem. Soc.*, **79**, 6563 (1957); (e) A. B. Burg and E. R. Birnbaum, *J. Inorg. Nucl. Chem.*, **7**, 146 (1958); (f) D. E. Burge, H. Freund and T. H. Norris, *J. Phys. Chem.*, **63**, 1069 (1959); (g) T. C. Waddington and F. Klanberg, *Naturwiss.*, **20**, 578 (1959); *J. Chem. Soc.*, 2329, 2332 (1960); (h) W. Kynastron, B. E. Larcombe and H. S. Turner, *ibid.*, 1772 (1960); (i) E. L. Muettterties, *J. Inorg. Nucl. Chem.*, **12**, 355 (1960).

(3) Lappert^{2c} has reported the preparation of pyridinium chloroborate but does not give experimental or analytical details.

(4) Generously supplied by the Shell Chemical Company.

chloroborate as white needles, m.p. 119–120°, ultra-violet spectrum (96% sulfuric acid)⁵: λ_{\max} 268 (shoulder), 273.5 (4350), 280 $m\mu$; 37.4% tropenium ion; calcd. for $C_7H_7BCl_4$: 37.38% tropenium ion. *Anal.*⁶ Calcd. for $C_7H_7BCl_4$: B, 4.44; Cl, 58.19; neut. equiv., 48.76. Found: B, 4.19, 4.28; Cl, 58.33, 58.33; neut. equiv., 48.99, 49.20. Reaction in cyclohexane (identical conditions) gives 6.0% tropenium chloroborate of 94.5% purity and 78.5% recovered cycloheptatriene. Reaction without solvent gives 16.1% tropenium ion and much polymer. Reaction in methylene chloride with *t*-butyl chloride co-catalyst (equimolar amount) gives 28.2% tropenium chloroborate of high purity.

Tropenium chloride with boron chloride gas in methylene chloride gives 34.0% tropenium chloroborate as white needles with slight enrichment of the chloride; found⁶: B, 4.40; Cl, 57.32; neut. equiv., 49.48; 38% tropenium ion.

Tropenium chloroborate (colorless single needles) is slightly hygroscopic; it dissolves slowly in water to give solutions of tropenium ion (λ_{\max} 275 $m\mu$ (4270))⁷ and boric acid. It sublimes to give unchanged chloroborate (major) and tropenium chloride (minor) in contrast to the bromoborate⁶ which gives only the bromide.

Wiberg⁸ reports a 1:1 complex of boron chloride and triphenylmethyl chloride (correct analysis, no m.p. below 200°); though not so identified, this was the first ionic chloroborate prepared. We find that boron chloride and triphenylmethyl chloride in methylene chloride give 78.8% triphenylcarbonium chloroborate, precipitated as yellow microcrystals by cyclohexane, visible spectrum (96% sulfuric acid):⁹ λ_{\max} 405, 432 $m\mu$ (38,200); 61.1% triphenylcarbonium ion; calcd. for $C_{19}H_{15}BCl_4$: 61.44%. *Anal.* Calcd. for $C_{19}H_{15}BCl_4$: B, 2.73; Cl, 35.85; $(C_6H_5)_3COH$, 65.74. Found:⁶ B, 2.40; Cl, 34.86; $(C_6H_5)_3COH$, 65.80 (m.p. 162° (reported:⁹ 162–2.5°)). This compound reacts instantly with cycloheptatriene in methylene chloride to give 100% tropenium chloroborate and 86.6% triphenylmethane. This rapid hydride exchange indicates^{3,6,10} that triphenylcarbonium chloroborate is an ionic salt and contains a BCl_4^- entity that can be transferred intact in a chemical reaction.

Conversion of cycloheptatriene (TrH) to tropenium (Tr^+) by metal halide with no co-catalyst may involve addition (1) followed by hydride transfer, or direct hydride abstraction (2). With co-catalyst ($A = R^-, H^-$; $B = -OH, -X$) route (3) or (4) may be followed.¹¹ In dry cyclohexane virtually no reaction occurs between cycloheptatriene and boron fluoride (0.58% tropenium formed)¹²

(5) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

(6) For methods of spectral and chemical analysis see K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

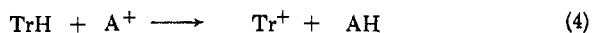
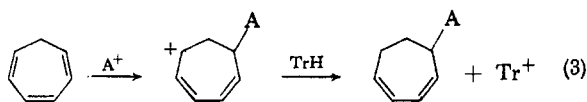
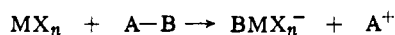
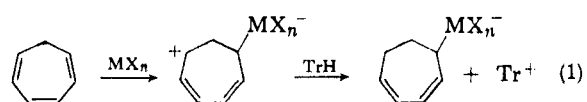
(7) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(8) E. Wiberg and U. Heubaum, *Z. anorg. allgem. Chem.*, **222**, 98 (1935).

(9) Hg. Frey, *Ber.*, **28**, 2517 (1895).

(10) (a) H. J. Dauben, Jr., and D. L. Pearson, Abstracts, 126th Meeting, American Chemical Society, New York, N. Y., Sept. 13, 1954, p. 18-O; (b) D. L. Pearson, Ph.D. Thesis, University of Washington, 1955.

(11) H. J. Dauben, Jr., K. M. Harmon, A. B. Harmon and L. R. Honnen, *J. Am. Chem. Soc.*, in preparation, will discuss these reactions and mechanistic paths in detail.



and stannic chloride (0.086% tropenium formed) in agreement with the failure of these halides to cause cationic polymerization without cocatalysts.¹³ Stannic chloride in dry methylene chloride gives 16.1% tropenium chlorostannate (white cubes from 12 *N* HCl, m.p. 252° (reported,¹⁴ 252°)). Water, hydrogen chloride, and *t*-butyl chloride¹⁴ increase the yield; however, in their absence methylene chloride must function as co-catalyst by reacting with stannic chloride to give a cationic species (not necessarily a free carbonium ion) which attacks cycloheptatriene. Stannic chloride and trianisylmethane in dry methylene chloride give only 0.35% trianisylcarbonium ion (λ_{\max} 485 $m\mu$ in 5% sulfuric acid)¹⁵ in 18 days. As trianisylmethane readily yields a stable cation through hydride loss,¹⁶ the cationic species derived from stannic chloride and methylene chloride fails to abstract hydride, and must attack cycloheptatriene by route (3) and not (4). Boron chloride converts trianisylmethane to the cation in cyclohexane (24.7%) and methylene chloride (8.5%), and thus-like boron bromide^{6,17} appears able to abstract hydride from an organic hydride donor. Methylene chloride appears to act as a co-catalyst in the cycloheptatriene–boron chloride reaction (presumably by route (3)) but this solvent hinders reaction with trianisylmethane where additive co-catalysis cannot be effective. This effect is most likely due to greater solvation (relative to cyclohexane) of boron chloride by methylene chloride.

Joy and Lappert¹⁸ report that boron chloride and cycloheptatriene give benzylboron dichloride. We find traces of aromatic material but have not iso-

(12) D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk, S. S. S. R.*, **113**, 339 (1957); *C. A.*, **51**, 14572f (1957), report tropenium ion formation and extensive polymerization when cycloheptatriene was heated with boron fluoride etherate; they attribute this to a reaction like (2) above. We feel their observations were caused by water co-catalyst since we observe no polymerization (quantitative recovery of cycloheptatriene) with BF_3 gas in dry cyclohexane; heating may have caused some polymerization in their case but this is doubtful in ether.

(13) (a) A. G. Evans and G. W. Meadows, *Trans. Faraday Soc.*, **46**, 377 (1950); (b) R. O. Colclough and F. S. Dainton, *ibid.*, **54**, 886 (1958).

(14) D. Bryce-Smith and N. A. Perkins, *Chemistry and Industry*, 1022 (1959).

(15) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(16) L. L. McDonough, Ph.D. Thesis, University of Washington, 1960.

(17) K. M. Harmon and K. D. Stevens, unpublished work; boron bromide in dry methylene chloride converts trianisylmethane to the cation in 77.5% yield in two days.

(18) F. Joy and M. F. Lappert, *Proc. Chem. Soc.*, 353 (1960).

lated benzylboron dichloride from these reactions or from the pyrolysis of the chloroborate. In the absence of details of their work we cannot account for the difference in products, but the isolation of 84.5% tropenium and recovered cycloheptatriene in our cyclohexane reaction indicates that aromatization is not a major factor under our conditions.

(19) American Chemical Society-Petroleum Research Fund Scholar, 1960.

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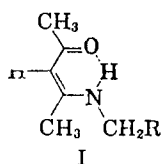
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RECEIVED JUNE 19, 1961

A NUCLEAR MAGNETIC RESONANCE STUDY OF KETO-ENOL EQUILIBRIA IN SCHIFF BASES. II
Sir:

A recent paper¹ presented evidence from proton magnetic resonance that bases derived from the 2:1 condensation of a β -diketone and a diamine are present in solution to an extent $\geq 95\%$ in the ketamine form with only a small dependence of the equilibrium on solvent. The $-\text{NH}-\text{R}$ structure was inferred from spin-spin splitting of the R methylene protons ($J = 6$ cps.) by N-H. This study now has been extended to bases derived from other monoamines and β -diketones in order to explore further the apparently high stability of the ketamine over the enol-imine tautomer.

Bases formed from monoamines and simple β -diketones such as acetylacetone give rise to proton resonance spectra similar to those derived from diamines. When $\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$ the compounds in CDCl_3 or CCl_4 solution exist in the ketamine form I as indicated by the vinyl signal at ~ 4.9 ppm.¹ and the splitting of the methyl or methylene protons into a doublet with $J \approx 5-6$ cps.



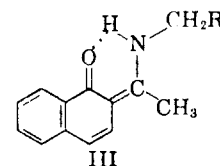
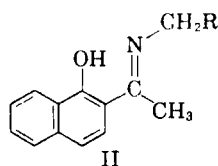
The benzyl base of dibenzoylmethane behaves similarly. No other signals attributable to the N-substituent were observable (concn. $\sim 0.4 M$) so that structure I is present to an extent $\geq 95\%$. There is no apparent solvent effect upon the equilibrium ($\text{CDCl}_3, \text{C}_6\text{H}_6, \text{pyridine}$).

These results, together with corroborative infrared studies on the above and related compounds,² offer further evidence of the greater stability of the ketamine form in aliphatic compounds as compared to either the ketimine or enol-imine tautomers. Accordingly, a search was made for other systems in which an alternate tautomer would be of comparable stability.

Derivatives of *o*-hydroxynaphthones were investigated. The tautomers II and III are possible for the base derived from 1-hydroxy-2-naphthone and a monoamine.

(1) G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 2099 (1961).

(2) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, *ibid.*, **71**, 3337 (1949).



When $\text{R} = \text{C}_6\text{H}_5$ the proton resonance spectrum in CDCl_3 has a sharp methyl signal at 2.37 ppm., complex aromatics at ~ 7 ppm., and at 16.5 ppm. the broad signal from the acidic proton (the acidic proton in acetylacetone enol is at 15.3 ppm. in C_6H_{12}). At 4.67 ppm. there is a field invariant doublet which collapses to a singlet upon deuteration of the acidic proton and is thus ascribable to the benzyl methylene group split by N-H with $J = 4.8$ cps. When $\text{R} = \text{H}$ the spectrum in either pyridine or CDCl_3 is analogous to that of the benzyl base. In CDCl_3 the methyl doublet is at 3.08 ppm. with $J = 4.4$ cps. In both compounds the stability of the keto-amine form with its chelated hydrogen-bonded ring (inferred in both cases from the presence of a highly unshielded proton) is sufficient to destroy the aromatic structure of one of the naphthalene rings. These results present some of the most direct physical evidence for such an effect. Previously, similar tautomerism in certain arylazonaphthols had been inferred from ultraviolet and infrared spectra.^{4,5,6} As expected, salicylalbenzylamine shows an unsplit methylene signal at 4.77 ppm. in CDCl_3 .

Preliminary studies of similar bases derived from 2-hydroxy-1-naphthone and 2-hydroxy-1-naphthaldehyde indicate that the phenol-imine form predominates. When $\text{R} = \text{H}$ in the former the N-methyl signal is a sharp singlet at 3.21 ppm. in CDCl_3 . The benzyl base of the aldehyde exhibits at 4.73 ppm. in CDCl_3 a broadened methylene resonance which persists in CCl_4 and pyridine.

These and other bases derived from *o*-hydroxynaphthaldehydes and *o*-hydroxynaphthones are presently under investigation and detailed results will be reported in the future.

Spectra were taken on a Varian HR-60 (at 60 or 15.1 Mc./sec.) or A-60 spectrometer using tetramethylsilane as an internal zero of reference. Bases were formed from the carbonyl compound and amine by standard procedures. Compounds were characterized by melting point or in the case of new compounds by elemental analysis. Financial support from the National Science Foundation is acknowledged.

(3) L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957).

(4) A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, 1443 (1953).

(5) E. Sawicki, *J. Org. Chem.*, **22**, 743 (1957).

(6) K. J. Morgan, *J. Chem. Soc.*, 2151 (1961), and references therein.

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RECEIVED AUGUST 16, 1961

THE STRUCTURE OF α -LUMICOLCHICINE—SOME EXAMPLES OF DIAMAGNETIC SHIELDING BY THE CARBON-OXYGEN DOUBLE BOND

Sir:

α -Lumicolchicine, which is formed with β -lumicolchicine and γ -lumicolchicine in the irradiation