TABLE II

ATTEMPTED RITTER REACTION

	Starting material	Nitrile	Product isolated	Remarks
1.	Methyldiphenylcarbinol[a]	Acetonitrile	IX	M.p. 143°. *Anal.* Calcd. for $C_{28}H_{24}$: C, 93.3; H, 6.7. Found: C, 93.1 H, 6.8
2.	Methyldiphenylcarbinol	Benzonitrile	IX	
3.	Methyldiphenylcarbinol	Chloroacetonitrile	IX	
4.	Methyldiphenylcarbinol	Hydrocyanic acid[b]	IX	
5.	Chloromethyldiphenylcarbinol[c]	Benzonitrile	1-Chloro-2,2-diphenylethylene	M.p. 41°.[d] *Anal.* Calcd. for $C_{14}H_{11}Cl$: C, 78.4; H, 5.1; Cl, 16.5. Found: C, 78.2; H, 5.0; Cl, 16.1
6.	Chloromethyldiphenylcarbinol	Acetonitrile	1-Chloro-2,2-diphenylethylene	
7.	Dichloromethyldiphenylcarbinol[e]	Benzonitrile	1,1-Dichloro-2,2-diphenylethylene	M.p. 77°. *Anal.* Calcd. for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.0; Cl, 28.5. Found: C, 67.4; H, 4.1; Cl, 28.4
8.	Methyldi(*p*-chlorophenyl)carbinol[f]	Benzonitrile	1,1-Di(*p*-chlorophenyl)ethylene	M.p. 86°.[f] *Anal.* Calcd. for $C_{14}H_{10}Cl_2$: C, 67.5; H, 4.0; Cl, 28.5. Found: C, 67.3; H, 4.1; Cl, 28.1
9.	Difluoromethyldiphenylcarbinol[g]	Benzonitrile	VIII (quant. yield)	M.p. 172° (from ethanol). *Anal.* Calcd. for $C_{21}H_{17}F_2NO$: C, 74.7; H, 5.0; N, 4.1; F, 11.3. Found: C, 74.6; H, 5.0; N, 3.8; F, 11.3

[a] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 226. [b] See ref. 5. [c] F. Bergmann and A. Kalmus, *J. Am. Chem. Soc.*, **76**, 4137 (1954). [d] W. P. Buttenberg, *Ann.*, **279**, 324 (1894). [e] M. A. Avy, *Bull. soc. chim. France*, [4] **49**, 12 (1931). [f] See ref. 11. [g] J. Bornstein, M. S. Blum, and J. T. Pratt, *J. Org. Chem.*, **22**, 1210 (1957).

acid was added to a mixture of 0.05 mole of the carbinol and 0.1 mole of the nitrile, each drop produced a red to violet color which faded quickly. The mixture was stirred and heated at 60–70° until an additional drop of acid no longer produced a color reaction (usually 15 min.). The mass was diluted with ice–water and the product filtered and crystallized from methanol or ethanol. The reaction of methyldiphenylcarbinol with hydrocyanic acid was carried out according to Mousseron, *et al.*[5]

Attempts to Deacetylate N-[1,1-Di(*p*-fluorophenyl)-2,2,2-trifluoroethyl]acetamide (as III).—The following reagents were tried, but without result: boiling trifluoroacetic acid at 100°, concentrated sulfuric acid at 25° during 3 days (although the solution turned yellow and fluorescent), sulfuric acid in boiling 75% acetic acid, and boiling ethanolic sodium hydroxide. Potassium hydroxide in boiling diethylene glycol appeared to lead to complete destruction of the molecule.

N-Benzhydrylacetamide (VI).—When 5.4 g. of V was refluxed for 3 hr. with a solution of 4 g. of sodium hydroxide in 100 ml. of anhydrous ethanol, one obtained, upon cooling, white crystals (3.8 g.) which were neutral and melted at 152°, as reported for VI.[15]

(15) A. Rahman and M. O. Farooq, *Rec. trav. chim.*, **73**, 423 (1954).

Dihydroazepinone Chemistry. III. The Base-Catalyzed Deuterium Exchange of 1,3-Dihydro-1,3,5,7-tetramethyl-2*H*-azepin-2-one[1]

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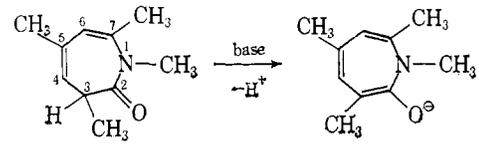
Received July 1, 1963

During the course of an extensive study of the chemistry of the dihydroazepinone ring system,[1,3] we were led to investigate the behavior of 1,3-dihydro-1,3,5,7-tetramethyl-2*H*-azepin-2-one (I)[1] with various basic reagents. Of particular interest was the possibility that, if enolization of the proton at position 3 (alpha to the carbonyl) could be made to occur, the unusual azepinoid anion II would result.[4]



I II

Prolonged treatment of I with potassium amide in liquid ammonia or with sodium hydride in dimethylformamide at 70° failed to consume these basic reagents, and I was readily recovered on appropriate work-up. However, addition of a solution of I in dry dimethyl sulfoxide (DMSO) to a hot (70°) solution of the methylsulfinyl carbanion ($Na^+{}^-CH_2SOCH_3$) in DMSO[5] produced a highly colored red-brown solution. The reaction mixture was stirred at this temperature for one hour, cooled, and treated with excess methyl iodide.[6] The deep color was discharged and a pale yellow mixture was obtained. Water was added and the product which was obtained by methylene chloride extraction proved, however, to be unchanged I (70+% recovery).

Despite the fact that I was not alkylated under these conditions, the deep color of the solution encouraged us to examine this reaction in greater detail. Treatment of the dihydroazepinone I with the methylsulfinyl carbanion prepared from sodium hydride and completely

(1) For paper II of this series, see L. A. Paquette, *J. Am. Chem. Soc.*, **85**, 3288 (1963).

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(3) Paper I, L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962), and future papers to be published.

(4) The negative charge of carbanions situated alpha to carbonyl functions almost exclusively resides on the more electronegative atom, oxygen. For a discussion of this subject, see J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chap. XI.

(5) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963).

(6) Several other alkylating agents were likewise employed with similar negative results.

deuterated dimethyl sulfoxide (CD_3SOCD_3), under conditions similar to those employed earlier, again gave a deeply colored solution. The color was discharged by the addition of a large volume of deuterium oxide. Extraction of the dihydroazepinone with methylene chloride and purification of the crude product by preparative gas chromatography gave a colorless liquid with the proper combustion analysis, and with an ultraviolet spectrum corresponding to I.

Nuclear magnetic resonance provided a means of establishing the extent and position of hydrogen–deuterium exchange of I. The n.m.r. spectrum[7] (Fig. 1) of compound I showed a low field singlet at 343

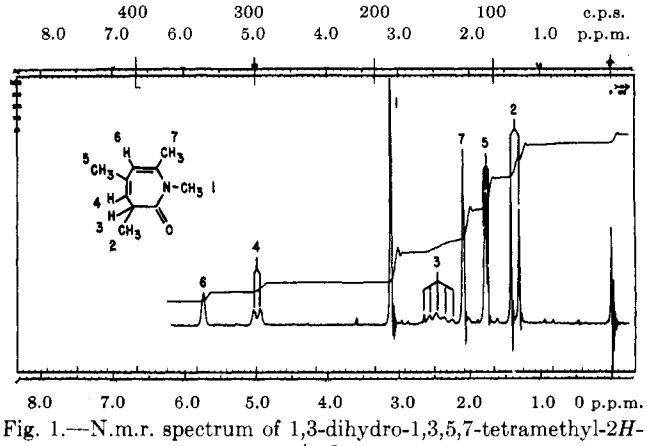


Fig. 1.—N.m.r. spectrum of 1,3-dihydro-1,3,5,7-tetramethyl-2*H*-azepin-2-one.

(proton at 6), a complex doublet (J = 4 c.p.s.) centered at 300 (proton at 4), and a complex 5-line pattern (J = 4 c.p.s.) centered at 148 c.p.s. (proton at 3).[8] In addition, the absorption peaks of the various methyl groups were located at 187 (singlet, 1-methyl), at 125 (singlet, 7-methyl), at 107 (triplet, J = 1.5 c.p.s., 5-methyl), and at 81.5 c.p.s. (doublet, J = 7 c.p.s., 3-methyl). On the other hand, the spectrum (Fig. 2)

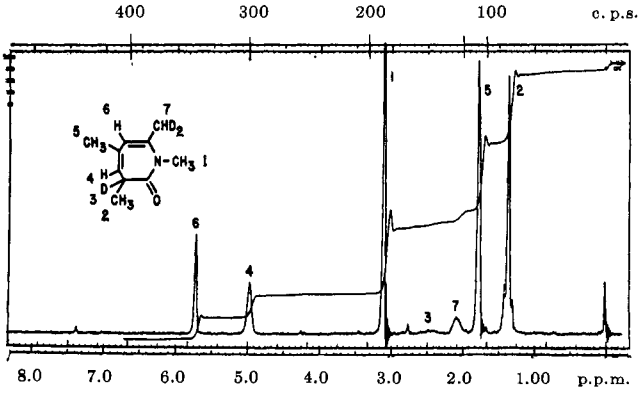
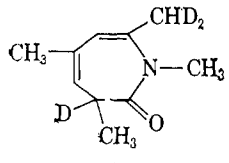
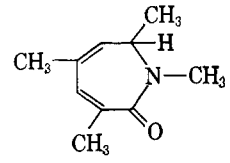


Fig. 2.—N.m.r. spectrum of deuterated product III.

of the deuterated product (III) indicates that the deuterium exchange had not affected the 1-methyl group (singlet, 187 c. p. s.) and the hydrogen at position 6 (singlet, 343 c.p.s.). That the proton at 3 had exchanged with deuterium was clearly demonstrated by the almost total disappearance of the peaks at 148 c.p.s. and the appearance of the 3-methyl as a singlet,[9] the 4-hydrogen as a singlet, and the 5-methyl as a singlet.[10] The novel aspect of the spectrum of III was the almost



III



IV

complete disappearance of the peak associated with the 7-methyl substituent at 126 c.p.s. The small residual broad absorption line[11] (area *ca.* 0.5 H) may be ascribed to incompletely deuterated moieties as $-CHD_2$ and $-CDH_2$.

These results clearly demonstrate the exchange of approximately four protons for deuterium and provide some insight as to the relative acidities of the various protons of I. The reluctance of the substance to undergo base-catalyzed alkylation indicates that its acidity is too low to provide reasonable equilibrium concentrations of anions even with strong bases. However, the protons at C-3 and of the methyl group at C-7 are acidic enough to allow exchange to occur.[12] In view of the lack of anion stabilization the possibility of distribution of the negative charge *via* 1,3-*trans* annular interactions seems remote. Finally, no isomerization of I to the carbonyl-conjugated system IV could be detected.

Experimental

A mixture of 500 mg. of 53% sodium hydride–oil dispersion (0.011 mole) and 10 ml. of completely deuterated dimethyl sulfoxide was heated at 100° for 1 hr. with stirring. The solution was allowed to cool to 70° and 1.65 g. (0.01 mole) of 1,3-dihydro-1,3,5,7-tetramethyl-2*H*-azepin-2-one was added. The solution was stirred at 70–75° for 2 hr. After cooling, 50 ml. of deuterium oxide was added, and the mixture was extracted with methylene chloride. The organic layer was washed with water and dried over magnesium sulfate. Evaporation of the solvent afforded a pale yellow oil from which residual traces of dimethyl sulfoxide were removed by preparative gas chromatography (4-ft. column, 20% silicone rubber on firebrick, 210°). The colorless oil thus obtained was flash-distilled before analysis; λ_{max}^{EtOH} 253 mμ (ε 4800); ν^{neat} 1670 cm.$^{-1}$ (amide carbonyl).

Anal. Calcd. for $C_{10}H_{12}D_2NO$: C, 72.69; H (and D); 9.15; N, 8.48. Found: C, 72.46; H (and D), 9.29; N, 8.14.

(7) Spectra were determined on dilute solutions in deuteriochloroform with a Varian A-60 spectrometer (tetramethylsilane, 0 c.p.s.).

(8) Careful examination of the sharp spike at the extreme left of this multiplet will show that a spin band off the resonance peak of the 1-methyl group overlaps this absorption peak.

(9) That 100% complete deuterium exchange had not occurred at position 3 is most evident in the weak residual lines of a doublet (compare Fig. 1) for the 3-methyl group.

(10) In Fig. 1, the 5-methyl group is a triplet (J = 1.5 c.p.s.) because of coupling with H-4 and H-6. Despite the fact that the environment of this substituent is not changed in III, this peak appears as a singlet (Fig. 2). We contend, after consideration of molecular models, that the introduction of the bulkier deuterium at H-3 has served to distort the dihydroazepinone ring sufficiently (because of the eclipsing of D-3 and H-4) to reduce the size of the coupling constant of H-4 and H-6 with the 5-methyl group to the point where it is difficultly resolvable.

(11) The broadening of this absorption line is produced by the small quadrupole moment associated with the deuterium atom: see L. M. Jackmann, "Nuclear Magnetic Resonance Spectroscopy," Pergammon Press Ltd., London, England, 1959, p. 80.

(12) The selective deuterium exchange at the 7-methyl substituent can only be rationalized on the basis of its proximity to the nitrogen atom.