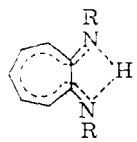
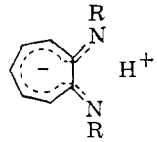


K



L

The fact that the aminoimines are more susceptible to attack by electrophilic reagents than tropolone is readily interpreted on the basis that the ring is more electronegative.[31] Thus, the compounds undergo bromination and chlorination in non-polar solvents to give single monosubstituted products in high yield. Furthermore, in contrast to tropolone,[3a,c] sulfonation[32] and nitration[33] are readily accomplished at room temperature. Lastly, the reaction with tetracyanoethylene to give a tricyanovinylaminoimine clearly is indicative of an addition–elimination reaction attributable to the electronegative character of the aminoimine. Under similar conditions tropolone gives a mixture of unidentified products.[22]

Acknowledgments.—The authors gratefully acknowledge the helpful discussions with Drs. E. G. Howard, W. H. Sharkey and B. C. Pratt. We are indebted to Dr. D. B. Chesnut and Dr. W. D. Phillips for determination and interpretation of several of the n.-m.-r. spectra. In addition, some of the n.-m.-r. spectra were determined by Mr. C. B. Matthews. We also wish to thank Miss Naomi E. Schlichter, Mrs. Judith Carberry and Miss Ellen Wallace for the determination and interpretation of the infrared and ultraviolet absorption spectra. Furthermore, we are indebted to Professor R. C. Lord of Massachusetts Institute of Technology for many helpful discussions of the infrared spectra.

(31) The fact that nitrogen is more capable of stabilizing a developing positive charge than oxygen may also be an important factor.

(32) Satisfactory analyses have not yet been obtained, but nuclear magnetic resonance studies have established that the 4-substituted derivative is formed.

(33) Unpublished result by Dr. A. D. Josey.

CONTRIBUTION NO. 601 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

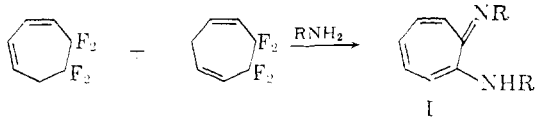
1-Amino-7-thioxo-1,3,5-cycloheptatrienes

BY W. R. BRASEN AND R. E. BENSON

RECEIVED JANUARY 26, 1961

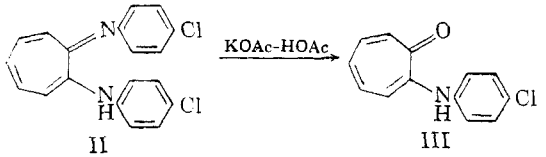
1-Amino-7-thioxo-1,3,5-cycloheptatrienes (IV), a previously unknown class of compounds, are accessible in good yields from the 1-amino-7-imino-1,3,5-cycloheptatrienes (I) by reaction with hydrogen sulfide. Although the thioxo compounds IV have considerable stability, they do not have the pronounced aromatic character associated with the aminoimines I.

The synthesis of 1-amino-7-imino-1,3,5-cycloheptatrienes was described in the previous paper.[1]



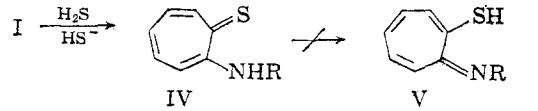
I

It was reported that the aminoimines were extremely stable to hydrolysis with strong acids or bases, but that a diaryl derivative II underwent hydrolysis readily in acetic acid in the presence of potassium acetate to yield the arylaminotropone III.



II III

Extension of the weak acid–weak base combination to the hydrogen sulfide–hydrosulfide system has given 1-amino-7-thioxo-1,3,5-cycloheptatrienes (IV), a previously unreported class of compounds.

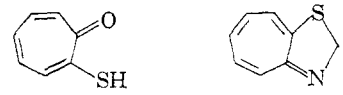


IV V

R = H, CH_3, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$

(1) W. R. Brasen, H. E. Holmquist and R. E. Benson, *J. Am. Chem. Soc.*, **83**, 3125 (1961); see also *ibid.*, **82**, 995 (1960), for preliminary note.

The most closely related compounds previously reported appear to be thiotropolone (VI) and its S-alkyl derivatives, prepared from 2-chlorotropone,[2]



VI VII

and derivatives of dihydro-1,3-thiaazulene (VII) synthesized from 2-chlorotropone and thiourea.[3]

Verification that the displacement reaction had proceeded without rearrangement was found in the formation of stable chelates from the thioxo derivatives IV with such metallic ions as copper, nickel and cobalt. Furthermore, the aryl derivative IV (R = $C_6H_4CH_3$-p) was converted to the corresponding aminoimine I by reaction with p-toluidine.

The aminothioxo derivatives IV are colored products that are readily soluble in dilute acid but insoluble in strong base, indicating that tautomerization to the iminomercaptocycloheptatriene structure V is not favorable, even under these conditions. This was verified by proton magnetic resonance studies of IV, R = CH_3. In contrast with the aminoimine I (R = CH_3) which shows a single methyl resonance,[1] the thioxo compound IV (R = CH_3) shows a doublet methyl resonance (3.05 and 3.16 p.p.m., tetramethylsilane reference). This

(2) T. Nozoe, M. Sato and K. Matsui, *Proc. Japan Acad.*, **29**, 22 (1953); **28**, 407 (1952).

(3) T. Nozoe, *Fortschr. Chem. Org. Naturstoffe*, **18**, 287 (1955).

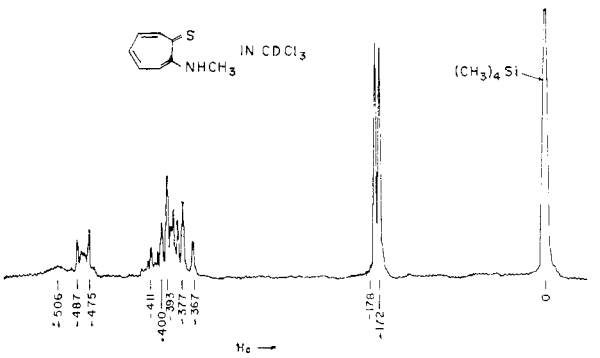


Fig. 1.—The n.m.r. data were obtained on a Varian Associates instrument HRS-60 operating at 56.4 megacycles and approximately 9400 gauss.

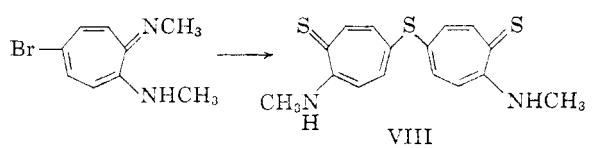
non-tautomerization of IV is similar to that observed for 2- and 4-mercaptopyridines as established by infrared spectral studies.[4]

Synthesis of the aminothioxo derivatives IV occurs readily when solutions of the aminoimines are heated with an excess of hydrogen sulfide. Hydrosulfide ion has in some instances been added as the sodium salt; however, this has been found to be unnecessary even when the reaction is carried out with the weakly basic N,N′-diarylaminoiminocycloheptatrienes.

The parent compound 1-amino-7-thioxo-1,3,5-cycloheptatriene was obtained directly in 60% yield from the tetrafluorocycloheptadienes without isolation of the intermediate 1-amino-7-imino-1,3,5-cycloheptatriene. This procedure avoided the troublesome isolation of the aminoimine, which was normally obtained in 30% yield. In the synthesis of N-substituted aminothioxo compounds IV, the intermediate aminoimines usually were isolated before treatment with hydrogen sulfide.

It is interesting to note that whereas 1-methylamino-7-methylimino - 1,3,5 - cycloheptatriene was inert to the potassium acetate–acetic acid hydrolysis system described for conversion of N,N-disubstituted aminoimines to N-substituted aminotropones, this aminoimine was converted readily to the corresponding aminothioxocycloheptatriene with hydrogen sulfide.

When a halogen-substituted aminoimine was employed in the synthesis, a bis-(aminothioxocycloheptatrienyl) sulfide VIII was isolated. Presum-

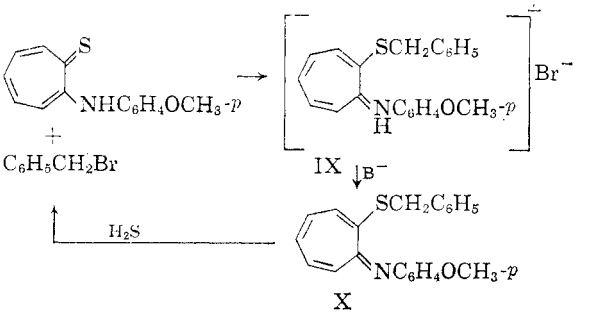


VIII

ably the reaction proceeds through intermediate formation of bis-(aminoiminocycloheptatrienyl) sulfide[1] which then undergoes a displacement reaction with sulfide ion to yield VIII.

(4) E. Spinner, *J. Org. Chem.*, **23**, 2037 (1958).

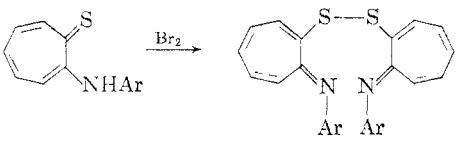
The N-arylaminothioxocycloheptatrienes resemble thiourea in that they are alkylated readily to yield S-alkyl salts IX. Unlike the thiouronium salts, treatment with base converts these S-alkyl derivatives to stable sulfides.



X

This expected alkylation of sulfur, rather than nitrogen, was verified by treatment of the sulfide X with hydrogen sulfide to produce the original aminothioxocycloheptatriene.

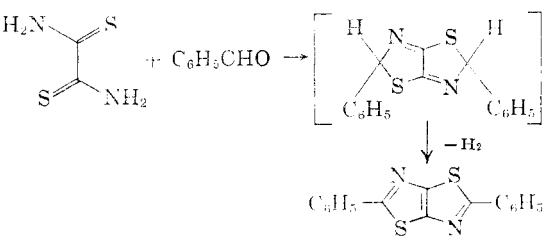
In contrast to the aminoiminocycloheptatrienes I, which are substituted in the nucleus by bromine, the aminothioxo compounds are oxidized readily to the disulfide by this reagent.



The resemblance of the aminothioxocycloheptatrienes IV to thioamides was further established by a reaction typical of dithioamides with aromatic aldehydes. Condensation of IV (R = H) with benzaldehyde yielded the dihydrothiaazaazulene XI

XI

which, unlike the products derived from dithiooxamide, is unable to undergo dehydrogenation.[5]



Experimental

1-Amino-7-thioxo-1,3,5-cycloheptatriene.—A fluorocarbon mixture of 6,6,7,7-tetrafluoro-1,3-cycloheptadiene (containing 42.5 g. of the cycloheptadiene) was added to a stirred solution of 300 ml. of anhydrous ammonia in 200 ml. of methanol during 1 hour. The mixture, containing suspended ammonium fluoride, was allowed to warm spontaneously to 5° and was then cooled to 0° by addition of more liquid ammonia. The sequence was repeated and

(5) John R. Johnson and Roger Ketcham, *J. Am. Chem. Soc.*, **82**, 2719 (1960).

the temperature finally allowed to rise to 20°. Anhydrous ether (500 ml.) was added, the mixture filtered, and the ammonium fluoride washed with ether. Ammonia and ether were removed from the filtrate at an aspirator (0–5°), thus reducing the volume to 250 ml. The solution was saturated with anhydrous hydrogen chloride with cooling. The precipitated ammonium chloride was removed by filtration, washed with 100 ml. of methanol, and the combined filtrates freed of solvent by distillation at reduced pressure at 0–10°. The semi-solid residue containing 1-amino-7-imino-1,3,5-cycloheptatriene hydrochloride was washed twice with ether by decantation and dissolved in 100 ml. of water. The resulting solution was diluted with 100 ml. of methanol and made slightly basic with a solution of 15 g. of sodium hydroxide in 50 ml. of water. The solution was saturated with hydrogen sulfide, heated to reflux, and hydrogen sulfide bubbled through the refluxing solution for 8 hours. Cooling of the solution precipitated a brown solid which was isolated by filtration. Recrystallization from methanol produced 21 g. (60%) of 1-amino-7-thioxo-1,3,5-cycloheptatriene, m.p. 137–138.5°.

Anal. Calcd. for C_7H_7NS: C, 61.27; H, 5.15; N, 10.21; S, 23.37; mol. wt., 137.2. Found: C, 61.20; H, 5.15; N, 9.94; S, 23.40; mol. wt., 122.

The infrared spectrum of this compound, unlike those of the N-substituted aminothioxo compounds, contained an NH band at 3.05 μ. The C=S absorption appeared at 9.6 μ. The ultraviolet spectrum had λ_{max} 448 mμ (ϵ 13,300) and λ_{max} 280 mμ (ϵ 20,700).

1-Methylamino-7-thioxo-1,3,5-cycloheptatriene.—A solution of 105 g. of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene in 300 ml. of methanol was saturated with hydrogen sulfide and heated to reflux. Hydrogen sulfide was bubbled through the refluxing solution during 17 hours, after which time this gas stream was replaced by nitrogen to sweep out most of the remaining hydrogen sulfide. Slow cooling of the solution yielded an orange-brown solid which was filtered off and taken up in 450 ml. of methanol. This solution was treated with decolorizing carbon, filtered, and cooled to yield 94 g. (88%) of 1-methylamino-7-thioxo-1,3,5-cycloheptatriene, m.p. 67–67.5°.

Anal. Calcd. for C_8H_9NS: C, 63.55; H, 6.00; N, 9.26; S, 21.20; mol. wt., 151. Found: C, 63.51; H, 6.00; N, 9.25; S, 20.87; mol. wt., 163.

The infrared spectrum showed no absorption in the region usually attributable to NH, and showed absorption at 9.63 μ (C=S), 3.25 and 3.3 μ (=CH), 3.45 μ (saturated CH), 6.25, 6.55 and 6.65 μ (conjugated C=C and/or C=N). The ultraviolet spectrum had λ_{max} 458 mμ (ϵ 10,300) and λ_{max} 285 mμ (ϵ 19,600).

To establish that the N-H absorption was obscured by the absorption attributable to saturated and unsaturated C-H, the methylaminothioxo compound was converted to the N-D derivative by refluxing with deuterium oxide containing a small amount of acid. Infrared examination of the resulting product showed strong absorption at 4.35 μ attributable to N-D. The remaining portion of the spectrum is very similar to that of the undeuterated product.

1-(*p*-Methoxyphenylamino)-7-thioxo-1,3,5-cycloheptatriene.—A stainless-steel pressure vessel of 500-ml. capacity was charged with 16.6 g. of 1-(*p*-methoxyphenylamino)-7-(*p*-methoxyphenylimino)-1,3,5-cycloheptatriene, 100 ml. of ethanol and 10 g. of hydrogen sulfide, and heated at 120° for 4 hours. The resulting dark red suspension was filtered, and the solid recrystallized from acetonitrile to yield 7.2 g. (60%) of 1-(*p*-methoxyphenylamino)-7-thioxo-1,3,5-cycloheptatriene, m.p. 132.5–133.5°.

Anal. Calcd. for $C_{14}H_{13}ONS$: C, 69.11; H, 5.38; N, 5.76; S, 13.18. Found: C, 69.01; H, 5.56; N, 5.74; S, 13.10.

The infrared absorption spectrum indicated no normal NH vibration. The principal absorption was at 9.7 μ (C=S), 3.25 μ (=CH), 3.55 μ (saturated CH), 6.2, 6.25, 6.6 and 6.7 μ (conjugated C=C and/or C=N). The ultraviolet absorption spectrum had λ_{max} 455 mμ (ϵ 8,000) and λ_{max} 285 mμ (ϵ 11,900).

1-(*p*-Tolylamino)-7-thioxo-1,3,5-cycloheptatriene.—A slow stream of hydrogen sulfide was bubbled through a refluxing solution of 30 g. of 1-(*p*-tolylamino)-7-(*p*-tolylimino)-1,3,5-cycloheptatriene in 100 ml. of *n*-butyl alcohol for 14 hours. The deep red solution was cooled and diluted with 200 ml. of ethyl alcohol and 300 ml. of ice-water to precipitate an orange-brown solid. The solid was taken up in 100 ml. of ethyl alcohol, treated with decolorizing carbon, filtered, and cooled slowly to yield 18.2 g. (80%) of orange needles of 1-(*p*-tolylamino)-7-thioxo-1,3,5-cycloheptatriene, m.p. 99–100°.

Anal. Calcd. for $C_{14}H_{13}NS$: S, 13.98; mol. wt., 227. Found: S, 14.14; mol. wt., 222, 229.

4,4-Bis-(1-methylamino-7-thioxo-1,3,5-cycloheptatrienyl) Sulfide.—A solution of 11.4 g. of 4-bromo-1-methylamino-7-methylimino-1,3,5-cycloheptatriene in 200 ml. of ethanol was refluxed for 16 hours while a stream of hydrogen sulfide was passed through the solution. The dark red solid which precipitated was isolated by filtration and recrystallized from methylene chloride–ethanol to yield 7 g. (65%) of the metallic, greenish 4,4′-bis-(1-methylamino-7-thioxo) sulfide, m.p. 166° dec.

Anal. Calcd. for $C_{16}H_{18}N_2S_3$: C, 57.79; H, 4.85; N, 8.43; S, 28.93; mol. wt., 332. Found: C, 57.97; H, 4.85; N, 7.70; S, 29.13; mol. wt., 367, 370.

1-Benzylthio-7-(*p*-methoxyphenylimino)-1,3,5-cycloheptatriene.—To a solution of 2.45 g. of 1-(*p*-methoxyphenylamino)-7-thioxo-1,3,5-cycloheptatriene in 30 ml. of acetonitrile was added 1.8 g. of benzyl bromide in 10 ml. of acetonitrile. The reaction mixture was allowed to stand for 10 minutes and was treated with 2 g. of triethylamine to precipitate an orange solid. Recrystallization of the solid from methylene chloride and methanol yielded 3.2 g. of 1-benzylthio-7-(*p*-methoxyphenyl)-imino-1,3,5-cycloheptatriene (91%).

Anal. Calcd. for $C_{21}H_{19}ONS$: C, 75.65; H, 5.71; N, 4.20; S, 9.62; mol. wt., 333. Found: C, 75.32; H, 5.93; N, 4.24; S, 9.49; mol. wt., 348.

Reaction of 1-Benzylthio-7-(*p*-methoxyphenylimino)-1,3,5-cycloheptatriene with Hydrogen Sulfide.—A stainless steel bomb of 500-ml. capacity was charged with 10 g. of 1-benzylthio-7-(*p*-methoxyphenylimino)-1,3,5-cycloheptatriene, 150 ml. of ethyl alcohol and 10 g. of hydrogen sulfide and heated for 4 hours at 120°. The product was a dark colored, tarry mixture from which only a small amount of crystalline material was isolated. This product proved to be 1-(*p*-methoxyphenylamino)-7-thioxo-1,3,5-cycloheptatriene and was identified by mixed melting point with authentic material.

Disulfide Formation from 1-(*p*-Methoxyphenylamino)-7-thioxo-1,3,5-cycloheptatriene.—An ice-cold solution of 0.8 g. of bromine in 20 ml. of methylene chloride was added to an ice-cold solution of 2.46 g. of the aminothioxo compound in 50 ml. of methylene chloride. The orange precipitate which formed was removed by filtration, dissolved in methanol and treated with 2 ml. of triethylamine. The resulting orange solid was crystallized from methylene chloride and ethanol to yield 2.1 g. (84%) of the disulfide VI, m.p. 159° dec.

Anal. Calcd. for $C_{28}H_{24}N_2S_2O_2$: C, 69.39; H, 4.99; N, 5.78; S, 13.23; mol. wt., 485. Found: C, 69.54; H, 5.04; N, 5.87; S, 13.30; mol. wt., 440.

2-(*p*-Chlorophenyl)-2H-cycloheptathiazole.—A solution of 1.37 g. of 1-amino-7-thioxo-1,3,5-cycloheptatriene, 1.41 g. of *p*-chlorobenzaldehyde and 1.5 ml. of concentrated hydrochloric acid in 20 ml. of ethanol was heated for 1 hour on the steam-bath. The initial deep red color faded to orange and cooling of the solution produced yellow needles. The cooled solution was diluted with water, the precipitate isolated by filtration and recrystallized from methanol and water. The yield of 2-(*p*-chlorophenyl)-2H-cycloheptathiazole was 1.7 g. (70%), m.p. 80.5–81°.

Anal. Calcd. for $C_{14}H_{10}NSCl$: C, 64.72; H, 3.88; N, 5.38; S, 12.34; mol. wt., 260. Found: C, 64.50; H, 3.97; N, 5.40; S, 11.83; mol. wt., 262.

Assignment of the cyclized structure to this compound was made principally on the basis of the infrared spectrum which did not contain the broad 9.6 μ C=S band which is present in the spectrum of the aminothioxo compound. The principal absorption was at 3.25 μ (=CH), 6.3, 6.45, 6.65, 6.7 and 6.8 μ (conj. C=C and/or C=N).

Metal Chelates of the Aminothioxo Compounds.—The copper chelate of 1-methylamino-7-thioxo-1,3,5-cycloheptatriene was prepared by combining a solution of 5 g. of the aminothioxo compound in 200 ml. of methanol with 200 ml. of an aqueous solution containing 3.5 g. of copper acetate

and 5 g. of sodium acetate. The brownish solid which precipitated was recrystallized from methylene chloride and ethanol to yield 5.1 g. (85%) of reddish-violet prisms, m.p. 190° dec.

Anal. Calcd. for $C_{16}H_{16}N_2S_2Cu$: S, 17.62; mol. wt., 364. Found: S, 17.68; mol. wt., 348, 354.

The copper chelate of 1-(*p*-tolylamino)-7-thioxo-1,3,5-cycloheptatriene was prepared by combination of a solution containing 2 g. of this material in 25 ml. of methylene chloride with 75 ml. of an aqueous solution containing 1.5 g. of copper acetate, 2 g. of sodium acetate and 25 ml. of ethyl alcohol. The methylene chloride was removed by distillation and the resulting violet precipitate was recrystallized from methylene chloride and ethyl alcohol to yield 2.5 g. (96%) of the chelate.

Anal. Calcd. for $C_{28}H_{24}N_2S_2Cu$: S, 12.42; mol. wt., 516. Found: S, 12.50; mol. wt., 665, 685.

The mercury chelate of 1-(*p*-tolylamino)-7-thioxo-1,3,5-cycloheptatriene was prepared by combining a solution of 2.27 g. of the aminothioxo compound in 20 ml. of ethyl alcohol with a solution of 2.7 g. of mercuric chloride in 20 ml. of ethyl alcohol. Addition of 2 g. of triethylamine precipitated a red crystalline solid which was recrystallized from methylene chloride and ethyl alcohol to yield 2.8 g. (85%) of the chelate, m.p. 166–167°.

Anal. Calcd. for $C_{28}H_{24}N_2S_2Hg$: S, 9.82; mol. wt., 653. Found: S, 9.98; mol. wt., 740, 750.

Amination of 1-(*p*-Tolylamino)-7-thioxo-1,3,5-cycloheptatriene.—A solution of 4.54 g. of the thioxo compound, 10.7 g. of *p*-toluidine (5 molar equivalents) and 100 ml. of 1-butanol was refluxed for 3 days under a slow stream of nitrogen. During this time, hydrogen sulfide could be detected in the effluent nitrogen stream. The solution was cooled and the precipitated solid was recrystallized four times from ethanol. The yield of 1-(*p*-tolylamino)-7-(*p*-tolylimino)-1,3,5-cycloheptatriene was 2.05 g. (33%). The melting point of this product with an authentic sample of the aminoimine was not depressed.

Acknowledgments.—The authors gratefully acknowledge the determination and interpretation of infrared and ultraviolet absorption spectra by Miss Naomi E. Schlichter and Miss Ellen Wallace, and of the n.m.r. spectra by Dr. D. B. Chesnut and Dr. W. D. Phillips. In addition, we wish to acknowledge the many helpful discussions of the infrared spectra with Professor R. C. Lord of Massachusetts Institute of Technology.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

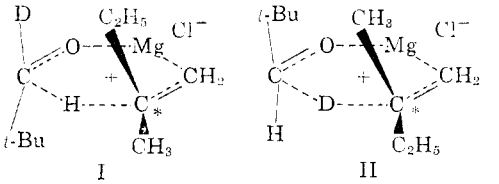
Asymmetric Reductions. X. Formation of Optically Active Neopentyl Alcohol-1-*d* by Asymmetric Grignard Reduction[1]

BY VICTOR E. ALTHOUSE, ERNA KAUFMANN, PAULA LOEFFLER, KANICHI UEDA AND HARRY S. MOSHER

RECEIVED DECEMBER 15, 1960

Trimethylacetaldehyde-1-*d* has been reduced by the Grignard reagent from (+)-1-chloro-2-methylbutane to give neopentyl alcohol-1-*d* which has the same configuration and 12% of the optical activity of the product from the reduction of this same aldehyde by actively fermenting yeast. Furthermore the reduction of non-deuterated trimethylacetaldehyde with the Grignard reagent from (−)-1-chloro-2-methylbutane-2-*d*, the deuterated enantiomorph of the above reagent, has given neopentyl alcohol-1-*d* with the same configuration and approximately 36% of the optical purity of the enzymically produced material. The absolute configuration of these products, the deuterium isotope effect and the relationship of this model chemical system to the enzymic system are considered.

Certain aspects of the asymmetric reduction of carbonyl compounds by optically active reducing agents[2] closely resemble those of enzymic reductions by the isolated alcohol dehydrogenase–diphosphopyridine nucleotide (ADH-DPNH) system[3] and by microbiological systems.[4] In the reduction of alkyl *t*-butyl ketones by the Grignard reagent from (+)-1-chloro-2-methylbutane[2] the extent of asymmetric reduction has been shown to depend upon the relative size of the alkyl and *t*-butyl groups. As the size of the alkyl group in this series of *t*-butyl ketones increases, the asymmetric bias of the reaction decreases, with the largest percentage asymmetric synthesis, 13%, being observed when the alkyl group was methyl. In this case (reduction of methyl *t*-butyl ketone) the transition state of lower energy leading to the preponderant isomer is symbolized by I where the deuterium atom is replaced by a methyl group.



The relationship between relative size of the groups on the ketone and the percentage asymmetric synthesis was not as simple in the alkyl phenyl ketones[5] nor the alkyl cyclohexyl ketones,[6] but there was excellent correlation in the purely aliphatic series represented by I where D was replaced by methyl through isobutyl.

For various reasons, including a desire to increase the asymmetric bias by increasing the difference in the steric effect of the R group and *t*-butyl group in the carbonyl compound, trimethylacetaldehyde-1-*d* (transition state I) was prepared and reduced by this same optically active Grignard reagent. Fur-

(1) We acknowledge with thanks the support of this investigation by a grant from the National Science Foundation and by research grant No. 5248 from the National Institutes of Health of the U. S. Public Health Service.

(2) See W. M. Foley, F. J. Welch, E. M. La Combe and H. S. Mosher, *J. Am. Chem. Soc.*, **81**, 2779 (1959), and references therein.

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