gave starting material in 90% recovery: mp 125–128° (lit.[8] mp 132–133°); mmp 129–131°.

Reaction of V with Phenylmagnesium Bromide in Tetrahydrofuran at 65°. Synthesis of 1-Cyclohexenyl Benzhydryl Ketone (VI).—The phenylmagnesium bromide from 10 g of bromobenzene and 5 g of magnesium in 50 ml of ether was decanted from excess magnesium. About half the ether was distilled off, 50 ml of dry tetrahydrofuran was added, and the solvent was distilled off until the boiling point reached 65°. A solution of 2.0 g of V in 15 ml of tetrahydrofuran was added. The mixture was refluxed for 20 hr. The brown reaction mixture was cooled in ice and 50 ml of water was added dropwise with swirling followed by 15 ml of concentrated hydrochloric acid. The resulting mixture was extracted three times with 20 ml of benzene. The combined benzene extracts were dried with $MgSO_4$ and evaporated. The solid residue was recrystallized from 30 ml of ethanol; yield, 1.2 g (60%); mp 124–126°; infrared spectrum (KBr) showed peaks at 6.03, 6.13, 6.89, 8.64, 13.44, and 14.28 μ; nmr (CS_2), τ singlet 2.85 (10), multiplet 3.08 (1), singlet 4.38 (1), doublet 7.80 and 8.45 (8).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.9; H, 7.3. Found: C, 86.9; H, 7.4.

Reaction of VII with Phenylmagnesium Bromide. Synthesis of 4-Triphenylvinyl-2,3-dihydrofuran (VIII).—The ether solution of phenylmagnesium bromide from 10 ml of bromobenzene, 5 g of magnesium, and 50 ml of ether was decanted from the unreacted magnesium. A solution of 2 g of VII in 70 ml of ether was added dropwise at 20°. The mixture was kept at 20° for 3 days. To the stirred and cooled reaction mixture was added dropwise 15 ml of water and 15 ml of concentrated hydrochloric acid. The organic layer was separated and dried over $MgSO_4$. The solvent was evaporated and the semisolid residue crystallized on treatment with ethyl acetate. The yield of yellow crystals was 1.4 g (60%), mp 129–131°. Further recrystallization from ethyl acetate raised the melting point to 137–138°. The infrared (KBr) spectrum showed peaks at 6.27, 6.70, 6.93, 8.51, and 9.65 μ; nmr (CS_2), τ multiplet 2.9 (15), triplet, 4.1 (1), triplet 5.8 (2), sextuplet 7.1 (2).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.8; H, 6.2. Found: C, 88.4; H, 6.2.

Synthesis of 2,3-Dihydrofuran.—The synthesis of 2,3-dihydrofuran was by a modification of the method of Paul.[15] A mixture of 22.5 g of a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol and 17.3 g of 2,5-dihydrofuran was heated in a sealed tube at 165–175° for 6 hr. The reaction mixture was distilled through a 9-in. Vigreaux column and the fraction boiling at 51–61° was collected. This material could be used without further purification in the next experiment, the preparation of VII.

Synthesis of 6,6-Diphenyl-2-oxabicyclo[3.2.0]heptanone-7 (VII).—Diphenylketene[17] (2.0 g) was mixed with 4 ml of the above mixture of the two isomeric dihydrofurans. The reaction mixture became warm and the color faded. The mixture was cooled and a white solid formed. The solid was recrystallized from ethyl acetate–ethanol: yield, 1.6 g (58%); mp 124–126°;[18] infrared (KBr), 3.35, 3.48, 5.63, 8.07, and 9.20 μ; nmr (CS_2), τ multiplet 2.8 (10), doublet 4.8 (1), triplet 6.2 (2), triplet with fine structure 6.8 (1), multiplet 8.1 (2).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 82.0; H, 6.1.

Synthesis of 6,6-Diphenyl-3-oxabicyclo[3.2.0]heptanone-7 (X).—A mixture of 6.7 g of diphenylketene[17] and 10 ml of 2,5-dihydrofuran was sealed in a glass tube under nitrogen. The tube was heated at 100° for 5 days, while the color faded to pale yellow. The tube was cooled in ice and the solid product was collected on a filter: yield, 4.6 g (51%); mp 123–124°[18] (the melting point was not raised on recrystallization from ethanol); infrared (KBr), 5.65, 6.70, 6.91, 8.75, 9.22, 9.40, and 11.08 μ; nmr (CS_2), τ multiplet 2.7 (10), multiplet 5.5–6.5 (6).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 82.1; H, 6.2.

Synthesis of 9,9-Diphenylbicyclo[6.2.0]decanone-10 (XI).—A mixture of 5.4 g of diphenylketene[17] and 20 ml of cyclooctene was heated at 100° under nitrogen in a tightly stoppered container for 40 hr. The color faded to pale yellow. The excess cyclooctene was evaporated under vacuum and the residue crystallized on addition of ethanol. The solid product was recrystallized from ethanol: yield, 5.5 g (74%); mp 94–95°; infrared (KBr), 3.35, 3.44, 5.64, 6.64, 6.77, and 6.85 μ; nmr (CS_2), τ multiplet 2.7 (10), triplet 6.8 (2), singlet 8.6 (12).

Anal. Calcd for $C_{22}H_{24}O$: C, 86.8; H, 7.9. Found: C, 86.9; H, 8.1.

(17) L. I. Smith and H. H. Hoehn, *Org. Syn.*, **20**, 47 (1940).

(18) The melting point of a mixture of VII and X was 98–113°.

Registry No.—VI, 4173-56-2; VII, 14002-01-8; VIII, 13958-56-0; X, 14002-02-9; XI, 13958-57-1; phenylmagnesium bromide, 100-58-3.

Hexahydro-1,3,5-trithia-6b-azacyclopenta[*c*,*d*]pentalene

RAYMOND C. FORT, JR., AND W. L. SEMON

Department of Chemistry, Kent State University, Kent, Ohio

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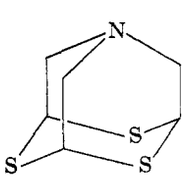
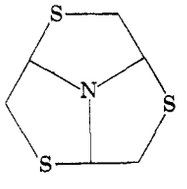
In 1955, Craig and co-workers reported[1] the isolation, as a by-product in the reaction of ammonium dithiocarbamate with chloroacetaldehyde hydrate, of a compound to which they assigned the adamantane structure I. The assignment was based upon elemental analysis and the infrared spectrum, which indicated the absence of NH or SH bonds and any multiple linkages. More recently, Thiel[2] has synthesized I by a relatively unambiguous route and found it to have properties different from those reported by Craig. Thiel was also able to obtain, from ammonia and mercaptoacetaldehyde, a second substance, seemingly identical with Craig's. Utilizing analysis and infrared spectra, he suggested structure II for this compound and submitted that it was this material which Craig had actually isolated.



I



II

Since these are isomeric compounds, and indeed, even give the same product, triethylamine, upon desulfurization with Raney nickel, the structure of II, and its identity with Craig's compound, have remained less than firmly established.

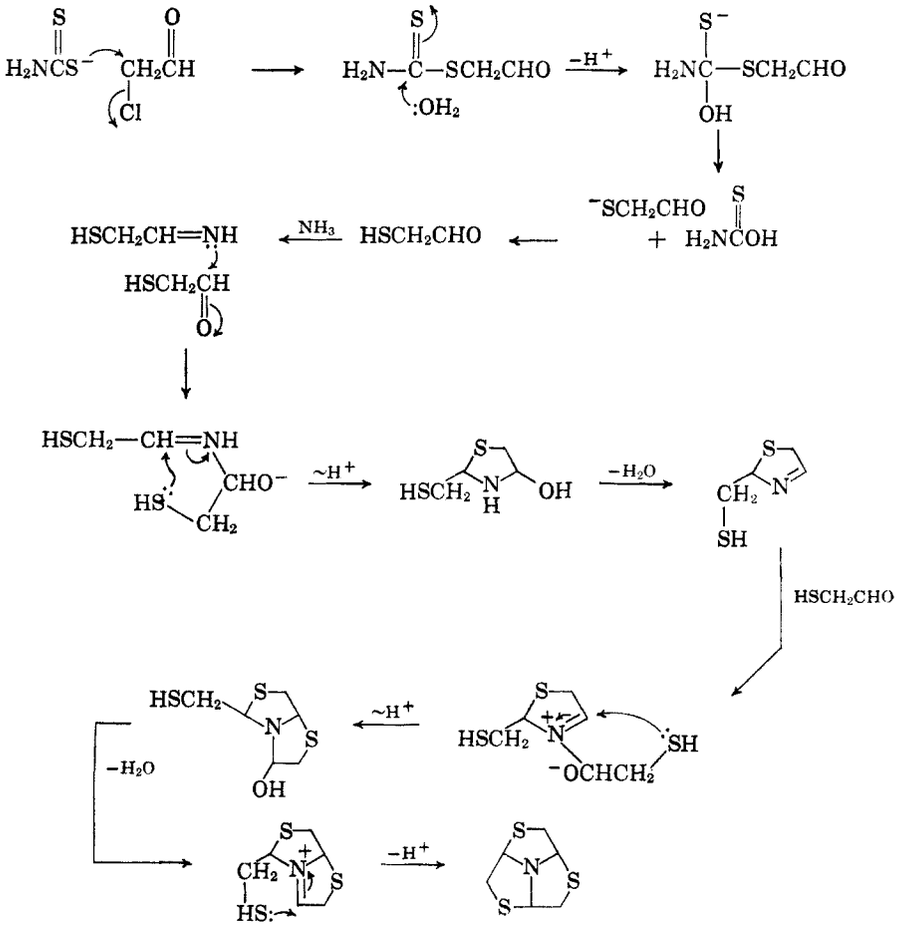
We have obtained a sample of Craig's *original* product,[3] and wish to report that its proton magnetic resonance spectrum confirms Thiel's assignment of structure II, the title compound. Spectra were run on approximately 1% w/v solutions of II in deuteriochloroform, benzene, and trifluoroacetic acid. The solutions in the first two solvents were maintained at 60° during observation to keep II in solution. Coupling constants were abstracted in each case by first-order analysis, and refined by hand computation. They are

(1) D. Craig, J. J. Shipman, A. Hawthorne, and R. Fowler, *J. Am. Chem. Soc.*, **77**, 1283 (1955).

(2) M. Thiel, F. Asinger, K. Schmiedel, H. Petschik, R. Haberl, and O. Hromatka, *Monatsh. Chem.*, **91**, 473 (1960); M. Thiel, F. Asinger, and K. Schmiedel, *Ann.*, **61**, 121 (1958).

(3) Dr. Craig is deceased. We wish to thank the B. F. Goodrich Co., Brecksville, Ohio, for providing us with this sample.

CHART I



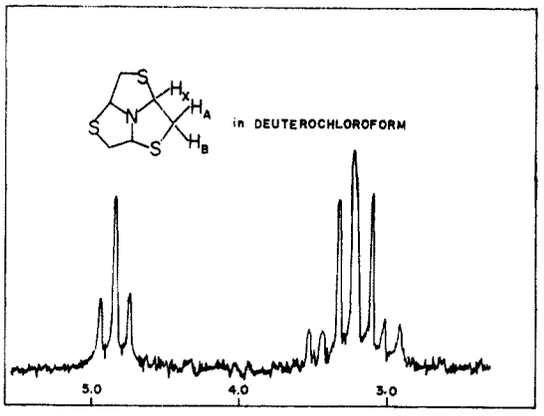


Figure 1.

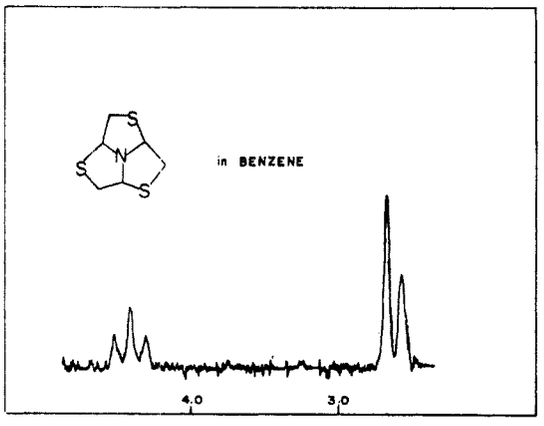


Figure 2.

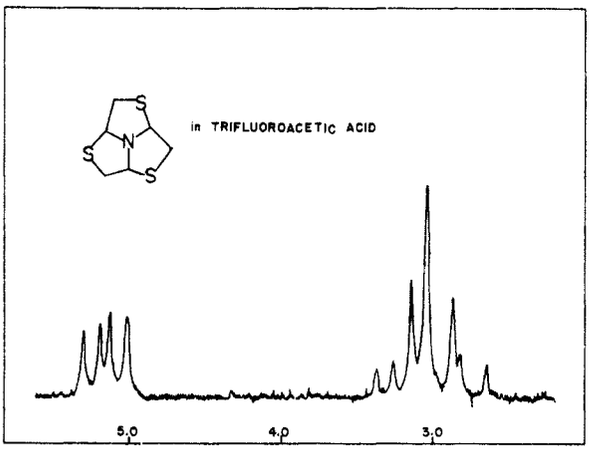


Figure 3.

reproducible to ±0.1 cps. In each solvent, integration confirmed the expected 2:1 ratio of methylene to methine hydrogens.

The 60-Mc spectrum of a $CDCl_3$ solution of II is shown in Figure 1. It clearly rules out the adamantane structure, and in conjunction with the earlier work, establishes II. The spectrum is of the ABX type, with the following parameters: J_{AB} = 11.5 cps, J_{AX} = 5.5 cps, J_{BX} = 6.1 cps, and δ_{AB} = 20.0 cps. The nonequivalence of the methylene protons is uniquely satisfied by II, which models show resembles a shallow dish. On the other hand, the symmetry of the adamantane, I, requires the methylene hydrogens to be equivalent. Furthermore, like other adaman-

tanes,[4] I is expected to display only very weak (*ca.* 2.5 cps) couplings.

Analysis of the spectrum is facilitated by examination of spectra obtained in benzene and trifluoroacetic acid solutions. Although the mechanism by which aromatic solvent-induced shifts are produced is in doubt,[5] there is no question of the considerable utility of this solvent. Figure 2 shows the spectrum of II in benzene; the nonequivalency of H_A and H_B has been removed, giving a close approximation to a first-order A_2X system, with apparent $J = 6.6$ cps.

Trifluoroacetic acid, which presumably protonates II on nitrogen, enhances the distinction between the methylene protons. As shown in Figure 3, the low-field peak, H_X, is now a quartet, the separation between the outermost lines ($|J_{AX} + J_{BX}|$) being 17.0 cps. The other parameters are $J_{AB} = 13.8$ cps, $J_{AX} = 6.6$ cps, $J_{BX} = 10.4$ cps, and $\delta_{AB} = 21.5$ cps. The changes in coupling constants are assumed to result from changes in bond lengths and angles, caused by the positive charge on nitrogen.

Thus, the spectra in all three solvents are consistent with the ABX interpretation, and therefore with the hexahydro-1,3,5-trithia-6b-azacyclopenta[*c*,*d*]pentalene structure.

It is interesting to speculate on the mechanism of formation of II. In Chart I we have outlined our suggestion,[6] based on the reaction reported by Thiel[2] between ammonia and mercaptoacetaldehyde. The ammonia required for the formation of the Schiff base may come from decomposition of the ammonium dithiocarbamate to CS_2 and NH_3 (a readily established equilibrium), or from ammonium chloride formed in the reaction $NH_2CS_2NH_4 + ClCH_2CHO \rightarrow NH_2CS_2CH_2CHO + NH_4Cl$.

We should like to point out also that II is capable of optical activity; we are presently engaged in attempts to separate it into enantiomers. Other chemical and spectroscopic studies of this interesting molecule are also in progress.

Registry No.—II, 5692-45-5.

(4) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).
(5) R. C. Fort, Jr., and T. R. Lindstrom, *Tetrahedron*, **23**, 3227 (1967).
(6) A referee has suggested an alternate mechanism, in which the cyclization is initiated by the attack of mercaptide ion from mercaptoacetaldehyde upon the Schiff's base. We regard the lifetime of this anion as short under the essentially neutral reaction conditions, and therefore prefer the mechanism of Chart I. A conclusive statement, of course, must await the results of our further studies.

Acylation of 5-Aminotetrazoles

FRED EINBERG

Pitman-Dunn Research Laboratories,
Frankford Arsenal,
Philadelphia, Pennsylvania 19137

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The formylation of aromatic amines by reaction with N,N-dimethylformamide and sodium methoxide was reported[1] to give good yields and to afford a simple, easily performed method. As part of our contin-

(1) G. R. Pettit and E. K. Thomas, *J. Org. Chem.*, **24**, 895 (1959); G. R. Pettit, M. V. Kalnins, T. M. H. Liu, E. G. Thomas, and K. Parent, *ibid.*, **26**, 2563 (1961).

TABLE I
ACYLATION OF 5-AMINOTETRAZOLES

Acylated tetrazole	Registry no.	Acylation method	Time of heating, hr	Product yield, %	Recrystallization solvent	Mp, °C[a]	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
5-Formamido	13958-60-6	$NaOCH_3$, DMF[b]	1.0	87.1	DMSO[b]	241 dec[c]	21.24	2.67	61.94	21.21	2.72	61.20
5-Formamido		HCOOH	4.0	89.7								
1-Methyl-5-formamido	14002-03-0	$NaOCH_3$, DMF	1.5	90.5	Absolute alcohol	140–142	28.35	3.97	55.10	28.11	4.24	55.01
1-Methyl-5-formamido		HCOOH	2.0	0.0								
2-Methyl-5-formamido	14002-04-1	$NaOCH_3$, DMF	1.5	50.8	Benzene	128–129	28.35	3.97	55.10	28.50	4.19	54.90
2-Methyl-5-formamido		HCOOH	2.0	80.0								
5-Acetamido	6158-77-6	$NaOCH_3$, DMAC[b]	3.0	47.6	Alcohol	277–278 dec[d]	28.35	3.97	55.10	28.52	3.99	54.92
5-Acetamido		Ac_2O	1.5[e]	51.2								
1-Methyl-5-acetamido	6154-02-5	$NaOCH_3$, DMAC	1.0	62.4	Methyl alcohol	166.5–167.5[f]	34.04	5.00	49.62	33.94	4.90	49.34
1-Methyl-5-acetamido		Ac_2O	2.0	37.1								
2-Methyl-5-acetamido	6154-06-9	$NaOCH_3$, DMAC	0.5	31.9	Water	152–153[g]	34.04	5.00	49.62	34.31	5.27	49.73
2-Methyl-5-acetamido		Ac_2O	2.0	27.1								
5-Benzamido	6158-74-3	$NaOCH_3$, DMBA[b]	0.75	94.7	DMF	281–282 dec[h]	50.79	3.73		50.75	3.88	
5-Benzamido		BzCl, NaOH, H_2O	1.0	10.6								
5-Benzamido		2BzCl, 2.1NaOH, H_2O[i]	2.0	20.1								
5-Benzamido		2BzCl, $2Na_2CO_3$, H_2O[i]	4.0	41.8								

[a] Melting points were measured with a Thomas-Hoover capillary melting point apparatus and were uncorrected. [b] DMF = N,N-dimethylformamide; DMAC = N,N-dimethylacetamide; DMBA = N,N-dimethylbenzamide; DMSO = dimethyl sulfoxide; BzCl = benzoyl chloride. [c] Evolved gas and turned plastic without discoloration at 241°, then resolidified and darkened above 300° without melting. [d] Lit.[4] 269° dec. [e] After 4.5 hr, 2-acetamido-5-methyloxadiazole was obtained in 51.8% yield, but no 5-acetamidotetrazole was obtained. [f] Lit. 164°, R. Stolle, K. Ehrmann, D. Rieder, H. Wille, H. Winter, and F. Henke-Stark, *J. Prakt. Chem.* **134**, 282 (1932). [g] Lit.[7] 153–154°. [h] Lit. 280° dec, L. E. Brady and R. M. Herbst, *J. Org. Chem.*, **24**, 922 (1959). [i] Numbers indicate number of moles.