as described for the D-galactose compound. After recrystallization from 15 parts of water by the gradual addition, at 0°, of two volumes of ethanol, the dihydrate showed $[\alpha]^{20}D$ +78.6° (*c* 2, water); literature +78°.[1,13] For analysis, the material was dried at room temperature in high vacuum over calcium chloride.

Anal. Calcd. for $C_6H_{11}K_2O_9P.2H_2O$ (372.4): C, 19.35; H, 4.06; P, 8.32. Found: C, 19.45; H, 4.17; P, 8.10.

(13) M. L. Wolfrom and D. E. Pletcher, *J. Am. Chem. Soc.*, **63**, 1050 (1941).

Acknowledgment. We thank the Analytical Services Unit of this laboratory, under the direction of Mr. H. G. McCann, for the analyses, and Dr. H. G. Fletcher, Jr., for helpful suggestions.

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Communications TO THE EDITOR

The Abnormal Claisen Rearrangement

Sir:

The "abnormal" Claisen rearrangement, *i.e.* the formation of *o*-(α,γ-dimethylallyl)phenol from γ-ethylallyl phenyl ether,[1] has generally been considered as a competitor to the normal Claisen rearrangement.[2] We wish to report evidence which proves this concept untenable, and shows conclusively that the formation of the abnormal product is due to rearrangement of the Claisen product, *o*-(α-ethylallyl)phenol. The experimental keystones of this conclusion are a kinetic examination of the rearrangement of γ-ethylallyl phenyl ether, and the preparation and rearrangement of *o*-(α-ethylallyl)phenol.

A 0.5 *M* solution of γ-ethylallyl phenyl ether[1] in *N*,*N*-diethylaniline was rearranged at 195 ± 1°. Samples withdrawn at intervals were taken up in petroleum ether and the diethylaniline removed by extraction with dilute hydrochloric acid. The product was analyzed for total phenol by infrared spectroscopy. After separation of phenolic material from residual ether, analysis for the normal and abnormal products was made via infrared measurements at 915 and 965 $cm.^{-1}$, respectively. A typical run is shown in Table I. While not sufficiently precise to warrant a detailed kinetic analysis, these data show clearly that the normal and abnormal products arise from consecutive processes.

Since the second rearrangement is slower than the first at 195°, lower temperatures permit easy isolation of the normal product. Thus heating a 1.0 *M* solution of γ-ethylallyl phenyl ether in mesitylene at 165° for 175 hr. gives *o*-(α-ethylallyl)phenol (b.p. 65° (0.25 mm), $n^{20}D$ 1.5321, ν 915 $cm.^{-1}$). When this phenol is heated in diphenyl ether, diethylaniline or neat at 200–225° it slowly rearranges to give *o*-(α,γ-dimethylallyl)phenol.[3] The earlier data[1] leading to this structure for the abnormal product are bolstered by the synthesis of a phenol with an identical infrared spectrum by the C-alkylation of dry sodium phenoxide with α,γ-dimethylallyl bromide in toluene.[4]

TABLE I

REARRANGEMENT OF γ-ETHYLALLYL PHENYL ETHER IN DIETHYLANILINE AT 195°

Time (hr.)	Ether (Mole/L.)	Normal Product (Mole/L.)	Abnormal Product (Mole/L.)
0	0.50	—	—
6	0.32	0.15	0.00
12	0.20	0.25	0.02
18	0.10	0.32	0.05
36	0.03	0.25	0.16
48	0.00	0.20	0.27

It is significant that the methyl ether of *o*-(α-ethylallyl)phenol [b.p. 80° (0.5 mm.), ν 907,990 $cm.^{-1}$] was recovered unaltered after being heated 13 hr. in diethylaniline at 195° or in diethylaniline containing one molar equivalent of phenol at 230° for 16 hr. Since the ether recovered from a partial rearrangement of γ-ethylallyl phenyl ether at 200° exhibited an unchanged infrared spectrum, α,γ-dimethylallyl phenyl ether is apparently not an intermediate. Furthermore, a sample of 2,6-dimethyl-4-(α-ethylallyl)phenol (undistilled, ν 910,-990 $cm.^{-1}$. Calcd. for $C_{13}H_{18}O$: C, 82.1; H, 9.5. Found: C, 82.8; H, 10.2), obtained by preferential

(1) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, **58**, 1388 (1936). C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

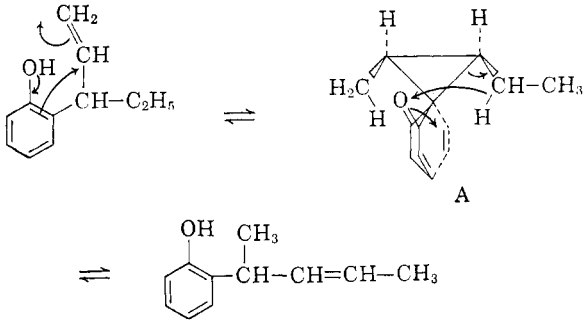
(2) *Cf.* for example D. S. Tarbell, *Org. Reactions*, II, 1 (1944). W. M. Lauer, G. A. Douldoras, R. E. Hileman & R. Lupino, *J. Org. Chem.*, 26, 4785 (1961).

(3) E. N. Marvell and J. L. Stephenson, *J. Org. Chem.*, 25, 676 (1960).

(4) N. Kornblum and A. P. Lurie, *J. Am. Chem. Soc.*, 81, 2705 (1959).

rearrangement[5] of a mixture of α- and γ-ethylallyl 2,6-dimethylphenyl ethers at 136°, was stable when heated 21 hr. at 215°.

These experiments show (a) that reaction depends on the phenolic hydroxyl, (b) that the reaction is intramolecular, and (c) that the geometric relation between the hydroxyl and the side chain is critical. This evidence is in accord with the mechanism shown here but does not uniquely demand it.



The intermediate A is related to a phenonium ion[6] and to the spirodienone isolated by Winstein and Baird.[7] Further studies aimed at the elucidation of mechanistic detail are in progress.

Acknowledgment. This work was supported by the National Science Foundation under grant NSF-G7342.

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(5) S. J. Rhoads, R. Raulins, and R. D. Reynolds, *J. Org. Chem.*, **76**, 3456 (1954).

(6) D. J. Cram, *ibid.*, **71**, 3863, 3875, 3883 (1949); **74**, 2159 (1952)

(7) S. Winstein and R. Baird, *ibid.*, **79**, 756, 4238 (1957)

Stereoselective Addition of Grignard Reagents to Unsaturated Azlactones[1]

Sir:

A number of pairs of geometric isomers of azlactones have been isolated.[2] Configurational assignments based on comparisons of physical properties have been made for these isomers.[3]

Previous work has shown that aryl Grignard reagents react with unsaturated azlactones (which possess an α,β-unsaturated carbonyl moiety) to give products of 1,2- addition, exclusively. Thus, 2-phenyl-4-benzylidene-5(4*H*)-oxazolone (I), m.p. 166°, obtained by Erlenmeyer condensation of benzaldehyde with hippuric acid, reacts with phenylmagnesium bromide to give 1,1-diphenyl-2-benzamidocinnamyl alcohol (II) and 2,5,5-triphenyl-4-benzylidene-2-oxazoline (III).[4] We now wish to report the 1,4- addition of aryl Grignard reagents to the isomeric unsaturated azlactones.

I was converted to its labile isomer, (IV) m.p. 149°, by treatment with 48% hydrobromic acid followed by saturation with hydrogen bromide.[5] We have prepared two other isomeric pairs of azlactones by this method—2-phenyl-4-(1-naphthylidene)-5(4*H*)-oxazolone and 2-phenyl-4-(*o*-methoxybenzylidene)-5(4*H*)-oxazolone.

When compound IV was treated with phenylmagnesium bromide, 2-phenyl-4-benzhydryl-5-oxazolone (V), m.p. 159°, was obtained in 40% yield. Lesser amounts of II (20%), III (10%), the products of 1,2-addition, and an uncrystallizable oil were also isolated. Compound V was identical with an authentic sample prepared by addition of benzene to I in the presence of anhydrous aluminum chloride.[6] The generality of this reaction was demonstrated by the observation that IV reacted with other aryl Grignard reagents, such as α-$C_{10}H_7MgBr$, *o*-ClC_6H_4MgBr, *p*-ClC_6H_4MgBr, and *o*-$CH_3C_6H_4MgBr$, to give 35–40% yields of the 1,4-addition products together with analogs of II. Moreover, we have observed in comparison experiments that compound I gives 1,2- addition products with these reagents (in yields of 70–75%), as well as oily substituted indenes.[4d] *The absence of any 1,4- addition products* was revealed by infrared spectral examination.

The formation of II and III from IV strongly suggests the isomerization of IV to I, followed by ring opening, since 1,2- addition to IV would give compounds isomeric with II and III.

This is the first example, to our knowledge, of a difference in chemical behavior of an isomeric pair of azlactones. The failure of I to give 1,4- addition products may be due to steric interference with formation of the postulated pseudo six membered ring. It is of interest to note that such 1,4- addition of the less bulky alkyl Grignard reagents to I has been reported.[7] We therefore tentatively suggest

(1) This research was supported by a grant (CY-4532) from the National Cancer Institute, National Institutes of Health, USPHS.

(2) (a) H. E. Carter and W. C. Risser, *J. Biol. Chem.*, **139**, 255 (1941). (b) W. Herz, *J. Am. Chem. Soc.*, **71**, 3982 (1949). (c) J. P. Lambooy, *J. Am. Chem. Soc.*, **76**, 137 (1954).

(3) R. E. Buckles, R. Filler, and L. Hilfman, *J. Org. Chem.*, **17**, 233 (1952).

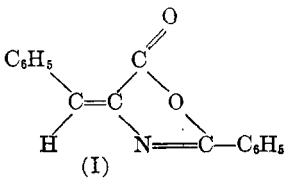
(4) (a) H. Pourrat, *Bull. soc. chim. France*, 828 (1955). (b) A. Mustafa and A. H. E. Harhash, *J. Org. Chem.*, **21**, 575 (1956). (c) R. Filler and J. D. Wismar, *J. Org. Chem.*, **22**, 853 (1957). (d) W. I. Awad and M. S. Hafez, *J. Org. Chem.*, **25**, 1180, 1183 (1960).

(5) S. Tatsuoko and A. Morimoto, *J. Pharm. Soc. Japan*, **70**, 2531 (1950); *Chem. Abstr.*, **45**, 1541 (1951).

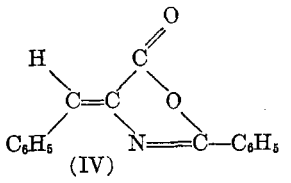
(6) (a) R. Filler and L. M. Hebron, *J. Org. Chem.*, **23**, 1815 (1958). (b) R. Filler and Y. S. Rao, *J. Org. Chem.*, **26**, 1685 (1961).

(7) L. Horner and H. Schwahn, *Ann.*, **591**, 99 (1955).

the following configurational assignments for I and IV.



(I)



(IV)

Further studies of the reactions of these compounds with organometallics and complex metal hydrides are in progress.

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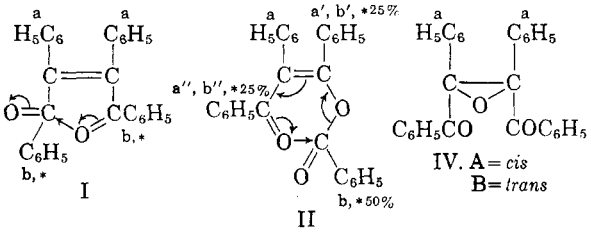
Oxidative Rearrangements of *cis*-Diaroylstilbenes. Tetraphenylfuran Peroxides and Dioxides. Aroyl-Group Migrational Tautomerism[1]

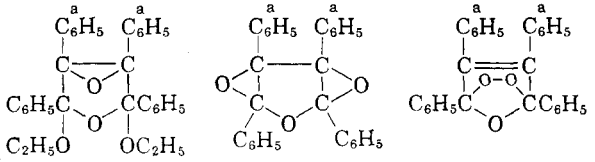
Sir:

Novel oxidative rearrangements were observed during studies on "*cis*-effects"[2] facilitating reactions of unsaturated 1,4-diketones. Chromic acid, hydrogen peroxide, perbenzoic acid (acetic acid), and ozone (CCl_4)[3] oxidized tetraphenylfuran to *cis*-dibenzoylstilbene (I, 40–80%) and thence to dibenzoylphenylmethane enol-benzoate (II, 10–20%).[4–6] Only chromic acid carried oxidation further to stereoisomeric enol-benzoate oxides III (A, 30%; B, 2%).[6] *cis*-Dibenzoylstilbene oxide IVA was isolated only from hydrogen peroxide reactions (4%; nonprecursor of II)[6]; its configuration was proved by reversible conversion to the new type cyclic ketal V.[6,7] Marked *cis*-effect was shown by the difficult oxidizability of *trans*-dibenzoylstilbene, only by chromic acid, to IVB (20%).[6] The novel ozonative rearrangement to an enol-benzoate suggests a similar step in other "abnormal" ozonolyses.[3c]



I II IV. A = *cis* B = *trans*

Symbols a, b, and * identify positions of labels when present: a, b = *p*-bromine; * = C^{14}-label.



V VIII a = *p*-Bromine labeled IX

Photooxidation of tetraphenylfuran[5c] in methanol (Methylene Blue) gave *cis*-dibenzoylstilbene and its cyclic dimethyl ketal (XIf, 30%)[6]; but in acetone it produced *cis*-dibenzoylstilbene oxide (IV, 15%) (*cf.* [7]), enol-benzoate II (14%), and a new type di-epoxide, VIII (43%), presumably through an unstable peroxide, IX.[8] One such peroxide, IXaa, was isolated; it underwent iodide reduction to Iaa and spontaneous conversion in the solid state into IVaa, IIaa′, and VIIIaa.

Novel sterically facilitated aroyl-group migration *via* arrows in II occurred during oxidative rearrangements of *p*-bromine-labeled *cis*-dibenzoylstilbenes Iaa and Ibb, respectively, to only one of the two tautomers possible in each case, presumably the more stable IIaa′ and IIbb′ rather than IIaa″ and IIbb″. Comparisons of ultraviolet absorptions with those of model compounds confirmed IIaa′ and were permissive for IIbb′. Conclusions were supported by syntheses of two *p*-bromine-labeled enol-benzoates where without such rearrangements

(1) Work supported in part by the National Science Foundation.

(2) (a) R. E. Lutz, R. G. Bass, W. J. Welstead, Jr., and C. L. Dickerson; a paper presented at the Southeast Regional ACS Meeting, Richmond, November 1959. Abstr. *The Bulletin*, Va. Section, ACS, **36**, 203 (1959). (b) R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, **81**, 3397 (1959). (c) R. E. Lutz and C.-K. Dien, *J. Org. Chem.*, **23**, 1861 (1958).

(3) Cf. Ozonation of 2,5-diphenylfuran: (a) P. S. Bailey and H. O. Colomb, *J. Am. Chem. Soc.*, **79**, 4238 (1957). (b) Ref. 2c.(c) P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

(4) Originally formulated as tribenzoylphenylmethane: (a) N. Zinin, *Zeit für Chem.*, 483 (1871); *Ber.*, **4**, 973 (1871); *Jahresber.*, 410 (1875). (b) J. Meisenheimer and K. Weibezan, *Ber.*, **54**, 3195 (1921); corrected in ref. 2a and 5.

(5) (a) F. M. Beringer, P. S. Forgione and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960). (b) H. H. Wasserman and A. Liberles; a paper presented at the Atlantic City ACS Meeting, September 1959, Abstr. p. 13P. (c) *J. Am. Chem. Soc.*, **82**, 2086 (1960).

(6) These experiments, except ozonations, were done prior to ref. 5b which stimulated efforts specifically to distinguish between the several possible mechanisms.

(7) *cis*-Dibenzoylstyrene oxide (VI, analog of IVA) was obtained (37%) upon photooxidation of 2,3,5-triphenylfuran in acetone and (8%) in ozonation of *cis*-dibenzoylstyrene. It was interconvertible with its cyclic diethyl ketal (VII, analog of V) which was first isolated but not formulated by P. S. Bailey, S. B. Mainthia, and C. J. Abshire [*J. Am. Chem. Soc.*, **82**, 6136 (1961)].

(8) (a) A cyclobutadiene monozonide. *Cf.* (b) G. O. Schenk, *Angew. Chem.*, **60**, 244 (1948). (c) **64**, 12 (1952). (d) G. O. Schenk, K. G. Kinkel, and H. J. Mertens, *Ann.*, **584**, 125 (1953). (e) G. O. Schenk, E. K. von Gutoff, K. H. Meyer, and W. Schauzer, *Angew. Chem.*, **68**, 304 (1956). (f) *Cf.* also C. E. Griffen and R. E. Lutz, *J. Org. Chem.*, **21**, 1134 (1956), and references cited. (g) J. Martel, *Compt. rend.*, **244**, 626 (1957).

TABLE I

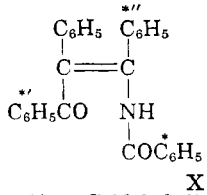
Compound[a]	M.P.	Analysis C	Analysis H	Absorption Maxima mμ[b]	Absorption Maxima ε × 10⁻³	Absorption Maxima μ[c]
Iaa	228–230	61.85	3.36	258	22.7	5.99
Ibb	224–225	61.85	3.33	268	23.1	6.00[d]
II	151–153	82.94	5.04	233[e]	31.6	6.02[g]
IIaa′	144–146	60.09	3.39	235[f]	34.4	6.00[g]
IIbb′	142–143	59.95	3.37	253	39.4	6.00[g]
IIIA	149–151	80.00	4.77	235	26.0	5.98[g]
IIIB	171–173	80.25	4.88	238	30.4	5.94[g]
IVA	172–173	83.12	4.99	251	27.3	5.91
IVAaa	170–171	58.73	3.56	250	19.3	5.90
IVB	166–168	83.33	4.89	253	29.0	5.91
V	200–201	80.42	6.51	None	—	None
VI[7]	92–94	80.24	5.07	254	26.2	5.92
VIII	155–158	82.73	4.83	226	25.6	None
VIIIa	149–151	59.79	3.21	226	36.5	None
IXa	100–150	59.74	3.42	—[h]	—	None
XIf	169–171	82.54	6.13	259	15.6	None
XIg	137–139	82.83	6.11	252	12.0	None

[a] Structures confirmed by appropriate reductions and/or hydrolyses. [b] In absolute ethanol. [c] Carbonyl bands, KBr pellet. [d] Bifurcated (6.05). [e] Shoulder 254 mμ, ε × 10⁻³ 22.0. [f] Shoulder 255 mμ, ε × 10⁻³ 27.0. [g] Ester carbonyl bands at 5.73–5.75 μ. [h] Not attempted because of instability in solution.

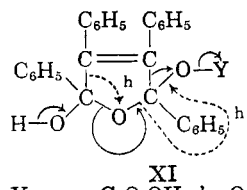
structural isomers should be produced, respectively, but which gave the same compound, presumably of the more stable type, non-*p*-bromine-substituted in the keto-phenyl group.

Chromic acid and hydrogen peroxide oxidations of *cis*-dibenzoylstilbene (I*) and photooxidation of tetraphenylfuran, C^{14}-labeled in the terminal phenyl groups, and ozonation of the resulting enol-benzoate samples II*, gave benzil containing 25% of the total C^{14}-activity. This proved scrambling with respect to the labeled phenyls (*25%) and the actuality but not point of occurrence of rearrangement. Ozonations of *p*-bromine-labeled enol-benzoates were shown to be unreliable for structure determination because pure IIbb′ gave both benzil and mono-*p*-bromobenzil, the products expected of of either rapid tautomerism or hybridization of IIbb′ and IIbb″ or of an intermediate ozone σ-complex.

Hydrazoic acid (Schmidt reaction) through a *cis*-effect oxidatively rearranged *cis* (but not *trans*) dibenzoylstilbene to keto enamine-benzoate X (42%) which had been first prepared by photooxidation of tetraphenylpyrrole.[5b] It showed red halochromism and freezing point lowering (i = 8.1)



X
(* = C^{14}-labeled)



XI
Y = a, CrO_2OH; b, OH; c $OCOC_6H_5$; d, O_2^+; e, OY = NHN_2^+; f, g, OH, OY = OCH_3; h = alternative path

in 100% sulfuric acid (83% recovery upon hydrolysis). Ozonation of samples made by the two routes, starting from I*, to benzil containing respectively half and none of the C^{14}-activity, proved the different C^{14}-locations X**′ and X**″ and excluded benzoyl-group migration and nitrogen-oxygen transpositional equilibration.

Oxidative rearrangements of *cis*-dibenzoylstilbene presumably involve primary *cis*-addition-cyclization. 2,5-Complexes XI[2a] are favored over 2,3 on steric grounds and analogy with known 2,5 cyclic ketals.[2b,9]

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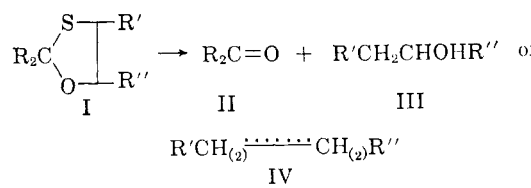
Received December 4, 1961

(9) NMR spectra interpreted by E. G. Brame show XIf and XIg to be stereoisomers of the 2,5 type, by the presence of only one kind of CH_3 line (R. E. Lutz and W. J. Welstead, Jr., *J. Org. Chem., in press*).

Studies in Organic Sulfur Compounds. XII.[1] Preparation of Inaccessible Enamine Amides by Desulfurization of Thiazolidines and Thiazolidinones[2]

Sir:

In earlier articles[3] we have shown that the Raney nickel desulfurization of cyclic hemithioketals (I) leads to ketones (II) accompanied either by the alcohol III or the hydrocarbon IV, depending upon the solvent used. The desulfurization of the nitrogen analogs, the thiazolidines,[4] and the related thiazolidinones[5] has been studied only infrequently and we should now like to report that the reaction can proceed reproducibly in an unexpected manner depending upon the selection of reaction conditions.



I II III

IV

(1) Paper XI, C. Djerassi and B. Tursch, *J. Org. Chem.*, 27, 1041 (1962).

(2) Supported in part by grant No. RG-6840 from the National Institutes of Health, U. S. Public Health Service.

(3) C. Djerassi, M. Shamma, and T. Y. Kan, *J. Am. Chem. Soc.*, 80, 4723 (1958) and earlier papers.

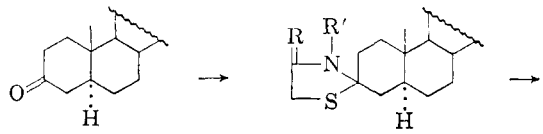
(4) *Inter al.*, H. T. Clarke, J. R. Johnson and R. Robinson, "The Chemistry of Penicillin," Princeton University Press 1949, chapter XXV (by A. H. Cook and I. M. Heilbron); W. A. Bonner and W. M. Reckendorf, *Ber.*, 94, 225 (1961).

(5) F. C. Brown, *Chem. Revs.*, 61, 463 (1961), especially p. 501.

The model ketone cholestan-3-one (V) was converted (β-mercaptoethylamine, benzene, *p*-TSA) into the thiazolidine VI (m.p. 136–137°, $[\alpha]_D$ +26° (all rotations in chloroform)), which was acetylated to VII (m.p. 171–172°, $[\alpha]_D$ +47°). Both VI and VII were found to be completely stable to prolonged refluxing in acetone with or without added base. Desulfurization of the *N*-acetylthiazolidine VII with W-2 Raney nickel catalyst (age: 7–32 days) in *benzene* solution provided over 50% of the *N*-acetylethylenamine (X) (m.p. 145–146°, $[\alpha]_D$ +61.5°), the structure of which was proved[6] by its NMR spectrum, by acid hydrolysis to cholestan-3-one (V) and by lithium aluminum hydride reduction to the extremely unstable oily enamine XIV (structure confirmed by infrared and mass spectra), which was hydrolyzed easily to V. Smaller amounts of XV and XVI accompanied the enamine X in the various benzene desulfurizations of VII. Desulfurization in *acetone* solution, on the other hand, provided as the predominant product the original ketone (*e.g.*, V), thus resembling the behavior of its oxygen analog I.[3] Analogous results were obtained with the six-membered homolog of VII, the *N*-acetyltetrahydrothiazane (m.p. 182–183°, $[\alpha]_D$ +44.5°), which produced *N*-acetyl-*N*-propylamino-Δ^2-cholestene (XI) (m.p. 128–129°, $[\alpha]_D$ +58.5°).

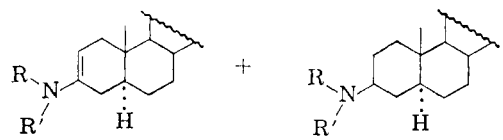
The generality of this approach to such hitherto unavailable enamines is substantiated by the following examples. Condensation of V with cysteine[7] followed by acetylation and diazomethane methylation led to VIII, which upon desulfurization with 15-day-old Raney nickel in benzene solution yielded 72% of the unsaturated enamine XII (m.p. 132–133°, $[\alpha]_D$ +53°). Similarly, reaction of cholestan-3-one (V) with thioglycolic acid and ammonium carbonate[8] produced in high yield two diastereoisomers of the 4-thiazolidinone IX (m.p. 264–265°, $[\alpha]_D$ +20.6° and m.p. 312–314°, $[\alpha]_D$ +26.6°), each of which was desulfurized with 14-day-old Raney nickel in benzene to afford 3-acetylamino-Δ^2-cholestene (XIII) (m.p. 214–215°, $[\alpha]_D$ +68°; cleaved by acid to V) together with 3β-*N*-acetylaminocholestane[9] (XVI) and cholestan-3-one (V) in an approximate ratio of 2:3:1.5. As expected, the latter was the principal product when the desulfurization was conducted in acetone solution.

The production of the saturated *N*-acetyl amine (*e.g.*, XV, XVI)—which appears to arise by an independent path rather than by further reduction of the enamine (*e.g.*, X, XIII)—is dependent on the age of the catalyst and this factor becomes more pronounced in the desulfurization of thiazolidines of simpler ketones. Thus desulfurization in benzene solution of the *N*-acetylthiazolidine of cyclopentanone with 3-day-old W-2 Raney nickel produces *N*-acetyl-*N*-ethyl-1-cyclopentene and *N*-acetyl-*N*-ethylcyclopentane in a ratio of 1:5, while with 30-day-old catalyst, this ratio is reversed to 8:1. Similar observations were made with the *N*-acetylthiazolidine or the 4-thiazolidinone derived from cyclohexanone.



V

VI. R = H_2; R′ = H
VII. R = H_2; R′ = Ac
VIII. R = $\lceil CO_2CH_3$; H; R′ = Ac
IX. R = O; R′ = H



X. R = C_2H_5; R′ = Ac
XI. R = C_3H_7; R′ = Ac
XII. R = $CH(CH_3)CO_2CH_3$; R′ = Ac
XIII. R = H; R′ = Ac
XIV. R = R′ = C_2H_5

XV. R = C_2H_5; R′ = Ac
XVI. R = H; R′ = Ac

The scope and mechanism of these desulfurizations will be discussed in detail in our full paper,[10] but there is little doubt that the presently described desulfurization reaction represents a rather general path to a variety of difficultly accessible enamines, a class of compounds which has recently gained considerable importance in organic chemistry.[11]

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(6) The Δ^3 location of the double bond was not excluded.

(7) S. Lieberman, P. Brazeau, and L. B. Hariton, *J. Am. Chem. Soc.*, **70**, 3094 (1948).

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(10) All of the new substances mentioned in the present communication were fully characterized in terms of elementary analysis, infrared, NMR, and mass spectra.

(11) See Symposium on Enamines, Abstracts of Div. of Organic Chemistry, pp. 44Q–46Q, 53Q–56Q, American Chemical Society Meeting, September 1961, Chicago, Ill.

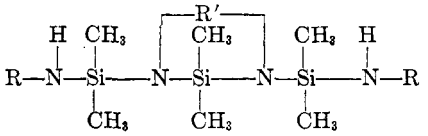
(12) Rockefeller fellow, 1961–1962, on leave from the University of Poznan, Poland.

Organosilazane Polymers[1]

Sir:

It is well known that ammonolysis of dihalodiorganosilanes yields mainly small ring compounds.[2] Although a series of patents describes the preparation of polysilazane polymers,[3-6] no high molecular weight compounds containing alternately ordered silicon and nitrogen in a linear polymer chain have been characterized in the literature.

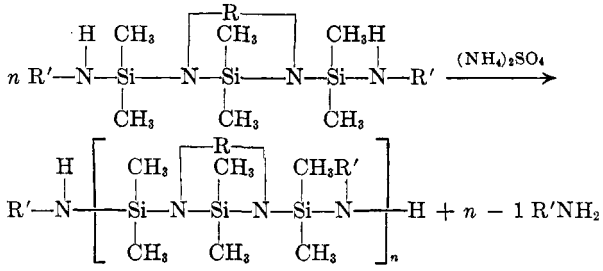
We wish to report that long chain silicon-nitrogen polymers may be formed in preference to ring structures when a halosilane derivative with a structure that sterically prevents the formation of small ring compounds is treated with ammonia or a primary amine and subsequently heated. Structures that undergo polymerization on heating include 1,5-diamino- or 1,5-bis(methylamino)trisilazanes, in which the nitrogen atoms in the 2- and 4-positions are bridged by an ethylene or a propylene group. For example:



I. R = H; R′ = $(CH_2)_2$
II. R = H; R′ = $(CH_2)_3$
III. R = CH_3; R′ = $(CH_2)_2$
IV. R = CH_3; R′ = $(CH_2)_3$

The monomers may be prepared by treating the chlorosilane intermediates, which have been described by Henglein,[7] with ammonia or methyl amine. In this manner, 1,5-bis(methylamino)-2,4-ethylene-1,1,3,3,5,5-hexamethyltrisilazane (III), b.p. 65–66°/0.14 mm., $n^{26}D$ 1.4582, d^{26}_4 0.9304, was obtained in a 66% yield. *Anal.* Calcd. for $C_{10}H_{30}N_4Si_3$: N, 19.28; Si, 28.99. Found: N, 19.17; Si, 29.12. The corresponding amino derivative (I) boiled at 69° at 0.29 mm. and has been obtained in yields up to 64%. Both aminosilane monomers (I and II) may be purified by rapid distillation at about 0.3 mm., but lose ammonia slowly on storage at room temperature to give compositions that approach the dimer. IV was obtained in a 65% yield, b.p. 84°/0.10 mm., $n^{26}D$ 1.4671, d^{26}_4 0.9542. *Anal.* Calcd. for $C_{11}H_{34}N_4Si_3$: N, 18.39; Si, 27.66. Found: N, 18.44; Si, 27.55.

Polymerization is effected with heat, but the rate of polymerization may be improved with catalytic amounts of ammonium sulfate.



In a typical experiment, 8.5 g. of freshly distilled 1,5-diamino-2,4-ethylene-1,1,3,3,5,5-hexamethyltrisilazane, 0.05 g. ammonium sulfate, and 10 ml. of xylene, heated at 140° ± 5°, ceased to evolve significant amounts of ammonia after 4 hr. The cooled polymer was treated with 10 ml. benzene, filtered, and the solvent was evaporated, leaving 7.7 g. (97% yield) of a soft tacky material. *Anal.* Calcd. for $[C_8H_{23}N_3Si_3]_n$: 39.12; H, 9.44; N, 17.11; Si, 34.32. Found: C, 39.20; H, 9.12; N, 16.91; Si, 34.62. Ebullioscopic molecular weight determinations in cyclohexane indicated average molecular weight above 5000, probably in the neighborhood of 8000. The polymer, which was a tacky, somewhat elastic solid, resembled an uncured gum rubber in many respects: It was soluble in nonpolar solvents such as cyclohexane, benzene, and carbon tetrachloride. A similar polymer was obtained when II was heated in the same manner. *Anal.* Calcd. for $[C_9H_{25}N_3Si_3]_n$: C, 41.64; H, 9.71; N, 16.19; Si, 32.46. Found: C, 41.30; H, 9.34; N, 16.28; Si, 33.02.

Additional evidence for the proposed structures was obtained from the infrared spectra of the monomers and polymers. Monomers I and II exhibited the two bands characteristic of primary amines in the 3500–3300 cm.$^{-1}$ region.[8] The free secondary amino group was indicated by a single band in the same region for III and IV. Spectra of the polymers prepared from I and II contained only a single absorption band near 3500 cm.$^{-1}$ reflecting the disappearance of the free amino group under polymerization conditions with the formation of the polysilazane structure.

The physical properties, infrared data, elemental compositions, and the molecular weights of the polymers offer strong evidence that polymerization occurs primarily through chain extension. The somewhat elastic properties may reveal a minor amount of crosslinking, but the maintenance of solubility in the higher molecular weight materials and the ratio of elements in final polymers indicate that side reactions are not significant.

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