bicyclic ring strain. Eastman and Freeman[20] have recently shown that the cyclopropane ring does not transmit conjugation when it connects a vinyl group with a carbonyl group. As yet no monocyclic compounds of the type $(CH_2)_n$—C=C—C=, in which n is 3 or 4, have been studied; so the effect (if any) of a strained substituent on an acyclic chromophore is not known. Hence, it is not certain whether the bicyclic structure is required to produce the bathochromic shift or whether the strained ring substituent is sufficient.

Experimental

Verbenone.—Verbenone was obtained from autoxidized α-pinene[21] by fractional distillation and subsequent purification through the semicarbazone, m.p. 208–209°. Hydrolysis of the semicarbazone by phthalic acid gave *l*-verbenone, $n^{20}\text{D}$ 1.4961, d^{20}_{4} 0.9731, $[\alpha]^{25}\text{D}$ $-253.5°$.

Verbenene.—Redistillation of the lower boiling fractions from autoxidized *l*-α-pinene gave *d*-verbenene, $n^{20}\text{D}$ 1.4997, d^{20}_{4} 0.8818, $[\alpha]^{25}\text{D}$ $+94.2°$.[22] Its identity was confirmed by comparison of the infrared spectrum with the spectrum of verbenene prepared by dehydration of verbenol by acetic anhydride.[23]

Pinocarvone.—Treatment of β-pinene in ethanol with selenium dioxide[24] gave an oil from which pinocarvarone was separated by way of the sodium bisulfite addition compound. Its identity is correct in accordance with the findings of Schmidt.[25]

The ultraviolet spectra were obtained on ethanol solutions using the Beckman Model DU spectrophotometer.

Acknowledgment.—The authors are indebted to Dr. J. P. Bain for the samples of myrtenal and nopadiene used in this study.

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[20] R. H. Eastman and S. K. Freeman, This Journal, **77**, 6642 (1955).

[21] A. Blumann and O. Zeitschel, *Ber.*, **46**, 1178 (1913).

[22] C. Paquot, *Compt. rend.*, **209**, 171 (1939).

[23] A. Blumann and O. Zeitschel, *Ber.*, **54**, 887 (1921).

[24] W. D. Stallcup and J. E. Hawkins, This Journal, **63**, 3339 (1941).

[25] H. Schmidt, *Ber. Schimmel & Co., Akt.-Ges.*, 56 (1941).

OLUSTEE, FLORIDA

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Nitration of Cyclic Ketones with Alkyl Nitrates[1]

BY HENRY FEUER, JAMES W. SHEPHERD AND CHRISTOS SAVIDES

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The nitration of cyclic ketones such as cyclopentanone, cyclohexanone, cycloöctanone and α-tetralone with alkyl nitrates in the presence of base affording the salts of cyclic α,α′-dinitro ketones has been investigated. The influence of base, reaction temperature, reaction time and mode of addition on the course of the reaction was studied and the yields of the salts were greatly improved.

The reaction of an alkyl nitrate with an active methylene compound in the presence of an alkali metal (or more frequently, an alkali metal alkoxide) to give the salt of a nitro compound with the nitro group attached to the active methylene group, has been known for many years.[2] However, very little work is reported on this nitration with cyclic ketones. Straus[3] and later Shriner[4] reported the nitration of α-tetralone and Wieland[5] extended the reaction to cyclopentanone and cyclohexanone.

The dinitration of cyclic ketones has been reexamined as part of a program to determine the scope of the reaction. Cyclopentanone was chosen as a model compound for the study of the effect of the reaction variables. This compound offered the advantage that its nitration product dipotassium 2,5-dinitrocyclopentanone (I) is not hygroscopic and can be purified readily. Since the nitration products of the other ketones turned out to be highly hygroscopic and difficult to purify, a suitable derivative had to be found on which the over-all yield could be based and which could be used for all the ketones which were nitrated. Conversion of compounds of type I to cyclic α,α′-dinitro ketones was unsatisfactory because the latter underwent decomposition with the evolution of oxides of nitrogen at room temperatures.[6] The tetrabromodinitro paraffins (II), which result from the reaction[7] of I with bromine in the presence of base, were found to be suitable derivatives. The yields throughout this investigation are expressed as II and are based on the starting ketone.

We found that the ring opening step gave a purer product if freshly prepared potassium hypobromite was employed as the brominating agent.

Compound I also was converted readily to 1,1,-4,4-tetrachloro-1,4-dinitrobutane with calcium hypochlorite.

In preliminary experiments, the nitration of cyclopentanone by the method of Wieland[5] (with ethyl nitrate and potassium ethoxide in a mixture of ethanol and diethyl ether) gave a low yield (7%) of II. The majority of the ketone was lost in the formation of tars, and if too large an excess of ethanol was used, the only product was a tar. These results indicate that the first step in the alkaline nitration reaction of cyclopentanone is the formation of the enolate anion. It seemed probable that the anion is an intermediate for both the nitration reaction and the self-condensation reaction which leads to the formation of tars. If this assumption were correct, it would be advantageous to employ: (1) a non-protonic solvent, (2) to use a stronger base than potassium ethoxide and (3) to

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[1] From the Ph.D. thesis of James W. Shepherd, Purdue University, 1954. Paper presented before the XIVth International Congress of Pure and Applied Chemistry, July 21–27, 1955, Zurich, Switzerland.

[2] For a thorough survey of the literature, reference is made to "The Chemistry of Nitrate Esters" by R. Boschan, R. T. Merrow and R. W. Van Dolah, *Chem. Revs.*, **55**, 485 (1955).

[3] F. Straus and W. Ekhard, *Ann.*, **444**, 146 (1925).

[4] R. L. Shriner and W. H. Horn, This Journal, **55**, 4652 (1933).

[5] H. Wieland, P. Garbsch and J. J. Chavin, *Ann.*, **461**, 295 (1928).

[6] 2,5-Dinitrocyclopentanone was stable only at Dry Ice temperature.

[7] K. Klager, *J. Org. Chem.*, **20**, 646 (1955).

find conditions in which the self-condensation of the ketone would be minimized.

Anhydrous diethyl ether was found to be a satisfactory reaction medium and was used throughout except during the investigation of solvent effects. Sublimed potassium *t*-butoxide was chosen because it is a stronger base than potassium ethoxide, and it has the additional advantage of being easily prepared in high purity and free from alcohol. When sublimed potassium *t*-butoxide was substituted in the reaction for ethanolic potassium ethoxide, the yield of II increased from 7 to 28%.

Amyl nitrate was found to be a satisfactory nitrating agent and was used for the majority of the experiments. Under similar conditions a 53% yield of II was obtained with ethyl nitrate and a 55% yield with amyl nitrate

Effect of Alcohol.—The adverse effect of added alcohol on a favorable equilibrium for the nitration reaction is demonstrated by the data shown in Table I. It is of interest to note that the amount of alcohol required to lower the yield drastically is relatively small. In fact, if it is assumed that in the nitration reaction, cyclopentanone is converted stepwise to the anion in the presence of two moles of potassium *t*-butoxide, the amount of alcohol which is added in experiment 4 is only 1.5 times larger than the amount of alcohol formed in the over-all reaction. In experiment 3, no alcohol was added and the yield was larger. These data indicate that one factor in the effectiveness of sublimed potassium *t*-butoxide, besides its being a strong base, might be its ability to form a stable complex[8] with *t*-butyl alcohol and therefore maintain a favorable equilibrium.

TABLE I

AMOUNTS OF INITIAL REACTANTS IN MOLES[a]

Expt.	Ketone	K *t*-OBu	*t*-Butanol alcohol	Yield, %
1	0.05	0.110	0.00	39.0
2	.05	.110	.110	15.5
3	.05	.165	.00	55.0
4	.05	.165	.15	17.0

[a] In expts. 1 and 2 the nitrate and ketone were added simultaneously to the base at −30°. In expts. 3 and 4 the ketone was added to the base followed by nitrate at −30°.

Effect of Temperature and Mode of Addition.—It seemed unlikely that the ratio of the rates of the self-condensation and nitration reactions would be the same at all temperatures. It was found that the self-condensation reaction was minimized at −30° and that no significant improvement in yield was obtained by further lowering of the reaction temperature, as shown in Table II.

The yield was also influenced by the mode of addition of the reactants and was highest when the ketone was added to the base first followed by the alkyl nitrate.

TABLE II

Temp., °C.	−20	−30	−40	−30	−30
Yield, %	28[a]	38[a]	36[a]	34[b]	44[c]

[a] Ketone and nitrate were added to the base. [b] Ketone was added to a mixture of nitrate and base. [c] Nitrate was added to a mixture of ketone and base.

Effect of the Rate of Addition of the Ketone.—The yield in the nitration of cyclopentanone varied with the rate of addition of the ketone to the base. Too slow addition would allow the anion initially formed to react with un-ionized ketone and lead to more self-condensation, while too rapid addition might lead to condensation of the newly added ketone with its anion before new ketone is ionized. That slow addition is unfavorable can be seen from the data in Table III. The yield for the simultaneous addition of ketone and nitrate is included for the purpose of comparison.

TABLE III

Addition of ketone, min.	75[a]	25[a]	10[a]	25[b]
Yield, %	42	48	46.5	38.5

[a] Ketone added to base (10% excess) followed by nitrate at −30°. [b] Nitrate and ketone added simultaneously to base (10% excess) at −30°.

Effect of Excess Base and Nitrate.—An increase in the amount of base in the reaction mixture might affect the over-all reaction in two ways. On one hand, the concentration of the enolate ion would increase and thereby the amount of self-condensation would be expected to decrease; on the other hand an excess of base might increase the amount of decomposition of the nitrate[2] and cause a lowering of the yield. The data in Table IV show that a maximum yield resulted with a 65% excess of base.

An increase in nitrate concentration from 10 to 50% did not affect the yield markedly.

TABLE IV[a]

Excess base, %	Excess nitrate, %	Yield, %
100	10	47.5
65	10	57.0
65	50	58.0
35	10	53.0
25	10	53.0
10	10	48.0
10	50	49.5

[a] In all expts., cyclopentanone was added to K *t*-OBu followed by amyl nitrate at −30°.

Effect of Reaction Time.—A study of the influence of the reaction time (see Table V) on the yield has revealed that it is most advantageous to work up the reaction mixture as soon as room temperature is attained.

TABLE V

Reaction time,[a, b] hr.	Excess base, %	Yield, %
16	65	57.0
4	65	60.0
0	65	62.0
16	10	48.0
4	10	52.0
0	10	54.8

[a] An additional one-hour period required to attain room temp. is not included. [b] In all expts. the ketone was added to the base followed by the nitrate at −30°.

Effect of Various Solvents.—The yield in the nitration was substantially increased when tetrahydrofuran was employed as the solvent. However, the same dependency on the concentration of base was observed in this reaction medium as in the

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(8) S. M. McElvain and L. R. Morris, THIS JOURNAL, **73**, 206 (1951).

case of diethyl ether. Thus the optimum yield of 72% was obtained with a 65% excess of base while a 10% excess gave only 62% of nitration. The high solubility of potassium *t*-butoxide in tetrahydrofuran, as shown in Table VI, might be responsible for its beneficial effect.

In general, the yields cannot be correlated with either the dielectric constant of the solvent or the solubility of the base in the solvent. Hexane, the poorest solvent for the base and having the lowest dielectric constant turned out to be a better reaction medium than toluene and almost as good as diethyl ether.

TABLE VI

Solvent	Solubility[a]	Dielectric constant at 20°	Yield,[b] %
Toluene	2.27	2.38[e]	21[c]
Hexane	0.27	1.89[e]	38[c]
Ether	4.34	4.34[e]	48[c]; 55[d]
Tetrahydrofuran	25.00	7.58[f]	62[d]

[a] Solubility of K *t*-OBu in g./100 g. solvent at 25–26°. [b] In all expts. the ketone was added to the base followed by nitrate at −30°. [c] The reaction time was 17 hr. [d] The reaction time was 1 hr. [e] A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," N.B.S. Circular 514, Aug., 1951. [f] F. E. Critchfield, J. A. Gibson, Jr., and J. L. Hall, THIS JOURNAL, **75**, 6044 (1953).

Effect of Different Bases.—Several bases were investigated, since it was expected that a stronger base than potassium *t*-butoxide would favor the nitration by shifting the keto–enolate equilibrium still further to the right. As seen from the data in Table VII none of the bases investigated proved superior to sublimed potassium *t*-butoxide. Here again we found, as had previous investigators,[9] that the nitration reactions gave lower yields with sodium bases than with potassium bases. It has been pointed out by Morton[10] that organo-alkalies, although of ionic character, are poorly dissociated in organic solvents. Hamell and Levine[11] suggested that this behavior would hold for alkali amides in organic solvents and that these compounds would also be present as ion pairs in solution. In the ion pair, the cation with a greater electron attracting ability would be expected to lower the effective basicity of the anion. This type of explanation was used to account for the lower yields obtained with lithium amide than with sodium amide in condensation reactions[11] and for the increase of the rates of reactions of organo-alkalies as the alkali metal is changed from lithium to sodium to potassium.[10] Carrying this over to our system, the lower yields in the nitration reaction with sodium bases probably result from both the lower basicity and the slower rate of reaction of the bases; the lower basicity decreases the amount of anion in the keto–enolate equilibrium and the slower rate of reaction leads to more self-condensation.

However, in view of the greater basicity of the bases which were studied the failure of both the sodium and potassium bases to give better yields than potassium *t*-butoxide is of interest. The approximate order of their relative strengths may be obtained from pK_a values of their conjugate acids as they appear on an arbitrary scale,[12] the base strength increasing as the pK_a increases. The pK_a values are: *t*-butyl alcohol, 19; N-methylaniline will have approximately the same strength as aniline, 27; triphenylmethane, 33; and ammonia,[13] about 34.

The low yield with sodium *t*-butoxide might also be due to the fact that in contrast to potassium *t*-butoxide it does not bind *t*-butyl alcohol.

There also is evidence that the low yield is in part due to decomposition of the nitrate by the strong base. When cyclopentanone was first treated with a molar equivalent of sodium amide to form the anion and a molar equivalent of sublimed potassium *t*-butoxide was added, followed by the addition of the nitrate, a higher yield of II was obtained than when only an excess of amide or triphenylmethylsodium was used.

TABLE VII[a]

Base	Excess base, %	Yield, %
$NaNH_2$	100	4.5
$NaNH_2$	10	8.4
$NaC(C_6H_5)_3$	65	9.0
$NaNCH_3C_6H_5$	10	10.0
Na *t*-OBu[c]	65	34.0[b]
$KNCH_3C_6H_5$	10	30.0
KNH_2	65	37.0
50% $NaNH_2$ + 50% KO*t*Bu	10	37.5
KO-*t*-Bu	10	48.0
KO-*t*-Bu	65	62.0, 72.0[b]

[a] In all expts. the ketone was added to the base followed by nitrate at −30° in ether. [b] The solvent was tetrahydrofuran. [c] Solubility in tetrahydrofuran 32 g./100 g.

After having established the best conditions for the nitration of cyclopentanone a number of other cyclic ketones were nitrated. The results are summarized in Table VIII.

Experimental

Dipotassium 2,5-Dinitrocyclopentanone.—A solution of 18.45 g. (0.165 mole) of sublimed potassium *t*-butoxide in 90 ml. of purified tetrahydrofuran was cooled with stirring to −30° by means of a Dry Ice bath, and 4.2 g. (0.05 mole) of cyclopentanone dissolved in 70 ml. of tetrahydrofuran was added dropwise over 30 minutes. A solution of 14.6 g. (0.11 mole) of amyl nitrate in 35 ml. of tetrahydrofuran was then added dropwise over 30 minutes with the temperature maintained at −30°. The reaction mixture was allowed to warm to 25°, with stirring, and filtered through a pressure filtration apparatus, using nitrogen as the pressure supplying gas. The residue, dipotassium 2,5-dinitrocyclopentanone, was washed successively with 70 ml. of tetrahydrofuran, 50 ml. of methanol and 50 ml. of ether and dried *in vacuo* over sulfuric acid.

Purification of Dipotassium 2,5-Dinitrocyclopentanone. Method A.—The above crude dry salt was dissolved in 30 ml. of water, reprecipitated by the addition of 150 ml. of methanol and dried over sulfuric acid at 50° (1 mm.). The yield of the purified product was 9.4 g. (75%), explosion point 259–261°. Explosion points were taken in a melting point block which was heated with an open flame so that the temperature rise was 20° a minute. The flame was removed as soon as the sample exploded and the explosion point was taken as the maximum temperature reached by the ther-

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(9) (a) W. Wislicenus and R. Grützner, *Ber.*, **42**, 1930 (1909); (b) R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1024 (1938).

(10) A. A. Morton, *Chem. Revs.*, **35**, 1 (1944).

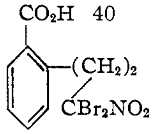
(11) M. Hamell and R. Levine, *J. Org. Chem.*, **15**, 162 (1950).

(12) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 50.

(13) S. Makishima, *J. Fac. Eng. Tokyo Imp. Univ.*, **21**, 115 (1938).

TABLE VIII

α,α,ω,ω-TETRABROMO-α,ω-DINITRO PARAFFINS [$(CH_2)_n-(CNO_2Br_2)_2$(I)] FROM CYCLIC KETONES

Ketone	I,[a] n	Yield, THF[b]	% in Et_2O	Formula	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Bromine, % Calcd.	Bromine, % Found
Cyclopentanone	2[c]	72	62	$C_4H_4N_2O_4Br_4$	99–100	...	...	..	..	..	..	...	...
Cyclohexanone	3[c]	53	..	$C_5H_6N_2O_4Br_4$	40–41	...	...	..	..	..	..	...	...
Cycloheptanone	4	54	44	$C_6H_8N_2O_4Br_4$	85–86	14.65	14.66	1.63	1.65	5.70	5.82	...	...
Cycloöctanone	5	35	..	$C_7H_{10}N_2O_4Br_4$	35–36	16.32	16.45	1.99	2.09	5.54	5.60	63.19	63.30
α-Tetralone		40	..	$C_{10}H_9NO_4Br_2$	127–128	44.50	44.49	2.96	3.01	5.18	5.20	29.62	29.53

[a] All compounds were crystallized from hexane.

[b] THF = tetrahydrofuran. [c] See ref. 7.

mometer after the flame was removed. Explosion points, taken in this manner, were reproducible to ±2°.

Anal. Calcd. for $C_5H_4N_2O_5K_2$: C, 23.95; H, 1.61; N, 11.19. Found: C, 22.85; H, 2.65; N, 11.06.

Method B.—A better method of purification consisted of recrystallizing the salt from 30% potassium hydroxide, washing the green needles with methanol until the filtrate became colorless and neutral and drying at 56° (1 mm.). The yield of the pure salt was 55%.

Anal. Found: C, 23.24; H, 2.03; N, 11.44.

1,1,4,4-Tetrabromo-1,4-dinitrobutane.—Dipotassium 2,5-dinitrocyclopentanone (9.4 g., 0.038 mole) purified by method A, was dissolved in 75 ml. of water and added rapidly at 0° to a solution of potassium hypobromite. The latter was prepared by adding dropwise 27.6 g. of bromine to a solution of 24.8 g. of potassium hydroxide (85% assay) in 150 ml. of water at 0°. The product was separated by filtration and recrystallized from hexane. The yield of 1,1,4,4-tetrabromo-1,4-dinitrobutane, m.p. 101–102° (lit. value[7] 100°) was 16.6 g. or 72%.

1,1,4,4-Tetrachloro-1,4-dinitrobutane.—A solution of 5 g. of purified dipotassium 2,5-dinitrocyclopentanone (0.02 mole) in 50 ml. of water was added rapidly to a solution of 12 g. of HTH (calcium hypochlorite) in 150 ml. of water at 0°. The reaction mixture was filtered and the filter cake was extracted with ether. The solvent was distilled off and the remaining product was then recrystallized from aqueous methanol yielding 4.54 g. (79.3%) of 1,1,4,4-tetrachloro-1,4-dinitrobutane, m.p. 50–50.5°.

Anal. Calcd. for $C_4H_4N_2O_4Cl_4$: C, 16.81; H, 1.40; N, 9.78. Found: C, 16.90; H, 1.47; N, 9.78.

Potassium *t*-Butoxide.—In a 500-ml. filter flask equipped with a Y-neck adapter to which a condenser surmounted by a calcium chloride drying tube was attached, 200 ml. of -butyl alcohol (distilled over sodium) was heated to reflux by means of an oil-bath. Potassium, 45.4 g. (1.16 mole), was added in small pieces, followed by 50 ml. of additional *t*-butyl alcohol and the reaction mixture was refluxed for 16 hours to assure complete reaction of the potassium. The excess *t*-butyl alcohol was evaporated at 120° (1 mm.) for four hours. The product obtained at this point titrated for 64% base, expressed as potassium *t*-butoxide. The solid cake was then purified by vacuum sublimation at 220° (1 mm.), in 30-g. portions, and 130 g. (72.5%) of 99% pure potassium *t*-butoxide was obtained.

Sodium *t*-Butoxide.—To 5.75 g. (0.125 mole) of sodium sand, prepared by the method of Fieser,[14] 70 ml. of *t*-butyl alcohol (distilled over sodium) was added in a 200-ml. flask. The reaction mixture was refluxed for 12 hours and the excess *t*-butyl alcohol was evaporated at 120° (1 mm.) for four hours. The crude sodium *t*-butoxide was purified by vacuum sublimation at 180° (1 mm.) to yield 20 g. (83%) of 99.5% pure sodium *t*-butoxide. Prior to sublimation it was found to be 99% pure.

Determination of Solubility of Potassium and Sodium Alkoxides.—A saturated solution of the sublimed alkoxide was prepared by shaking an excess amount of the alkoxide with the purified solvent, for 12 hours at 25°. The suspension was allowed to settle, and a portion of the clear supernatant liquid was transferred under dry nitrogen pressure to a flask. The solvent was evaporated *in vacuo*, the residue was dissolved in distilled water and aliquots of the aqueous solution were titrated with standard hydrochloric acid to phenolphthalein end-point.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work and to the Ethyl Corporation for a generous gift of amyl nitrate.

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(14) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 368.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE R. B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Synthesis and Reactions of Brominated N-Methylolamides[1]

BY HENRY FEUER AND JAKE BELLO

RECEIVED MARCH 28, 1956

The bromination of N-methylolacrylamide (I) gives the normal addition product N-methylol-2,3-dibromopropionamide (II) while that of N-methylolmethacrylamide (III) results in the unexpected formation of N,N'-methylenebis-(2,3-dibromoisobutyramide) (IV) instead of N-methylol-2,3-dibromoisobutyramide (V). The latter has now been prepared by bromination of methacrylamide followed by methylolation under basic conditions. In the dark, in the complete absence of acid, compound V is converted to IV by bromine, but not by iodine. It is proposed that compound V is an intermediate in the conversion of III to IV.

Previous work in this Laboratory[2] has shown that the reaction of bromine with N-methylolmethacrylamide (III) gave N,N'-methylenebis-(2,3-dibromoisobutyramide) (IV) instead of the expected N-methylol-2,3-dibromoisobutyramide (V). In contrast, bromination of N-methylolacrylamide (I) gave the normal addition product, N-methylol-2,3-dibromopropionamide (II).

The formation of N,N'-methylenebisamides by condensing an amide with formaldehyde in an acidic medium has been known for a long time.[3]

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(1) This paper was presented before the Division of Organic Chemistry at the New York City Meeting of the American Chemical Society, September 15, 1954.

(2) H. Feuer and U. E. Lynch, THIS JOURNAL, **75**, 5027 (1953).

(3) G. Pulvermacher, *Ber.*, **25**, 318 (1892).