with sodium bicarbonate and the solution was extracted with ether. When the ether was dried and evaporated, 4.0 g. of white solid, VII, was obtained, (29%). Upon recrystallization from acetone–water, this material melted at 160–160.5°.

1,3-Di-*p*-tolyl-5,5-dimethyl-6-piperidinohydrouracil (V).—A mixture of *p*-tolyl isocyanate (13.30 g., 0.10 mole) and 1-piperidinoisobutene (6.95 g., 0.05 mole) was sealed in a thick-walled tube and heated at 110–120° for 20 hr, then at 150° for 3 hr. The glassy solid was taken up in hot acetone to remove it from the tube. Upon evaporation of the acetone, an oil was obtained which did not solidify. The oil was taken up in dry ether and hydrogen chloride gas was passed into it. The hydrochloride precipitated as a white hygroscopic solid. This hydrochloride was then dissolved in a mixture of 3 g. of sodium hydroxide in 15 ml. of methanol and 100 ml. of water. This solution was then stirred with ether for 1.5 hr. After separation, the ether was washed with water, then dried over magnesium sulfate, and evaporated. The residual oil (20 g., 98%) solidified after standing for a week. After several recrystallizations from aqueous acetone, the resulting white solid had m.p. 157–158°; $\lambda_{\max}^{\text{Nujol}}$ no peaks in 3-μ region, 5.81 (s), 5.94 (s), and 6.18 (w) μ. Elemental analysis was performed on the picrate. To a solution of 0.526 g. of V in 3.0 ml. of methanol was added 3.0 ml. of a saturated (at 24°) picric acid solution. The mixture was warmed for 5 min. on a steam bath, then allowed to stand at room temperature overnight. The solid obtained on filtration was washed with ethanol, then recrystallized from ethanol, yielding material with m.p. 170–171°.

Anal. Calcd. for $C_{31}H_{34}N_6O_9$: C, 58.67; H, 5.40; N, 13.24. Found: C, 58.96; H, 5.54; N, 13.27.

1,3-Dimethyl-5,5-dimethyl-6-hydroxyhydrouracil (VIII). A. Preparation from IV.—To a solution of 40 ml. of hydrochloric acid and 10 ml. of water was added 7.6 g. (0.0201 mole) of IV. The solution was then refluxed for 17 hr. After the reaction mixture had cooled, it was filtered and 6.1 g. (97%) of material with m.p. 216–220° was obtained: several recrystallizations from aqueous acetone raised this to 228–231°; $\lambda_{\max}^{\text{Nujol}}$ 2.85 (m), 5.75 (s), 5.97 (s), and 6.24 (w) μ; $\lambda_{\max}^{\text{CH}_3\text{CN}}$ 2.87 (m), 5.75 (s), and 5.91 (s) μ; and τ (CH_3CN) 2.65 c (10 H), 5.20 (1H), 7.78 (1H, hydroxy), 8.48 (3H), and 8.68 (3H). Upon warming, new peaks appeared in the infrared at 2.85 and 6.12 μ.

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.57; H, 5.89; N, 9.29.

B. Preparation of III (Hydrochloride).—To a solution of 10 ml. of hydrochloric acid and 15 ml. of water was added 1.7 g. of the hydrochloride of III. The solution was refluxed for 42 hr., then cooled and filtered. The solid obtained after being washed with ether had m.p. 223–225°. The weight obtained was 1.15 g. (82%). The infrared spectrum was identical with that of VIII prepared from IV. After recrystallization from dimethylformamide it melted at 228–230°. The mixture melting point with material VIII derived from IV was unchanged.

1,3-Di-*p*-tolyl-5,5-dimethyl-6-hydroxyhydrouracil (IX).—To a solution of 50 ml. of hydrochloric acid and 20 ml. of water was added 12.0 g. (0.0296 mole) of V. The reaction mixture was refluxed for 12 hr. The solid obtained after cooling and filtering weighed 7.6 g. (0.0225 mole, 76%). This material was pure enough to be used directly in the next step.

1,3-Diphenyl-5,5-dimethylbarbituric Acid (X).—To a solution of VIII (1.0 g., 3.18 mmoles) in 40 ml. of methylene chloride was added a solution of 3.3 g. (0.011 mole) of sodium dichromate dihydrate and 3.6 g. of sulfuric acid, diluted to 10 ml. with water. After addition, the two-phase system was stirred for 20 hr. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated. A white solid was obtained (86%) which, after recrystallization from aqueous acetone, had m.p. 230–232°; $\lambda_{\max}^{\text{Nujol}}$ no peaks in 3-μ region, 5.64 (w), 5.80 (s), 5.85 (s), and 6.24 (w) μ; and τ (CCl_4) 2.57 c (10H), 8.25 (6H).

1,3-Di-*p*-tolyl-5,5-dimethylbarbituric Acid (XI). A.—To a solution of 3.0 g. (.87 mmoles) of IX in 40 ml. of methylene chloride was added slowly with stirring and cooling a solution of 6.6 g. (0.022 mole) of sodium dichromate dihydrate and 8.0 g. of sulfuric acid, diluted to 20 ml. with water. After addition, the two-phase system was stirred for 24 hr. Using the isolation procedure described for compound X, 2.1 g. (70%) of the desired product XI was obtained. After recrystallization from ethanol–water, it had m.p. 164–165°; $\lambda_{\max}^{\text{Nujol}}$ no peaks in 3-μ region, 5.64 (w), and 5.83 (s) μ; and n.m.r. (CCl_4) typical AB pattern from *p*-tolyl peaks at τ 2.78, 2.91, 3.02, and 3.15 (8H), 7.64 (6H), and 8.37 (6H).

Anal. Calcd. for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.26; H, 5.92; N, 8.11.

B.—A solution of 1.32 g. of dimethylmalonic acid (0.010 mole) in 20 ml. of dry tetrahydrofuran was mixed at room temperature with a solution of 4.44 g. of N,N′-di-*p*-tolylcarbodiimide (0.020 mole) in 25 ml. of dry tetrahydrofuran. No precipitate came out of solution after 30 min. at room temperature, so the reaction mixture was warmed for 10 min. on a steam bath and a white solid began to come out of solution. The reaction mixture was allowed to stand at room temperature for 6 hr., with warming on a steam bath for 5 min. after 2 hr. and after 4 hr. At the end of 6 hr., the reaction mixture was chilled briefly, then filtered. The solid residue was washed several times with cold tetrahydrofuran, then dried, yielding 1.3 g. of di-*p*-tolylurea with m.p. 268–269°. The reaction mixture was evaporated and the solid obtained was recrystallized from ethanol-water. Insoluble material and the first two crops of crystals were all di-*p*-tolylurea. In all, 2.3 g. (95%) of this material was obtained. The third crop of crystals weighed 1.3 g. (38%) and, after a recrystallization from ethanol–water, had m.p. 164–165°. The melting point and infrared and n.m.r. spectra of this material XI (B) were identical with those for XI (A) and for a mixture of XI (A) and XI (B).

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Lithiated Diamines as Metalating Agents

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Lithium metal reacts with diamines to give lithiated derivatives. Such lithiated diamines can be used to metalate a variety of weakly acidic compounds. In general, the metalation products form 1:1 complexes with the diamines. The corresponding sodium series has also been studied.

In a previous publication[1] we reported the ready preparation and isolation of N-lithioethylenediamine by the reaction of lithium metal powder with ethylenediamine in an organic solvent. We further showed that, once formed, N-lithioethylenediamine could be used as a metalating agent in its reaction with acetylene to produce a stable lithium acetylide–ethylenediamine complex.

We now wish to report that both of the above reactions are general. Lithium metal powder reacts with a variety of diamines to give lithiated derivatives which can be used to metalate a variety of weakly acidic compounds.

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[1] O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **28**, 2775 (1963).

TABLE I

REACTION OF N-LITHIOETHYLENEDIAMINE WITH AMINES AND HYDROCARBONS[a]

Amine or hydrocarbon	LiEDA, mole	Amine or hydrocarbon, mole	Solvent	Time, hr.	Temp., °C.	Yield, %	Color
Aniline	0.380	0.390	Ether	3	−10	91	Colorless
Aniline	0.380	0.390	Toluene	3	25	93	Colorless
Diphenylamine	0.380	0.390	Toluene	2.5	25	93	Colorless
N-methylaniline	0.380	0.390	Toluene	3	25	91	Colorless
Ethylacetylene	0.560	0.800	Hexane	2	25	95	Colorless
Phenylacetylene	0.120	0.130	Ether	5	25	98	Red
Fluorene	0.360	0.370	Ether	6	25	94	Yellow
Indene	0.370	0.380	Ether	2	−10	85	Pale green
Indene	0.370	0.380	Toluene	3	25	95	Pale green

[a] The lithiated species in all cases formed an ethylenediamine complex.

N-Lithioethylenediamine reacts smoothly with a variety of amines and hydrocarbons at room temperature. In general the product isolated is a 1:1 crystalline solid complex of the lithiated derivative with ethylenediamine (see Table I).[2]

$$RH + NH_2CH_2CH_2NHLi \rightleftarrows RLi\cdot NH_2CH_2CH_2NH_2 \quad (1)$$

There is one exception to the above generalization. If acetylene is introduced into a slurry of N-lithioethylenediamine above the decomposition temperature of lithium acetylide–ethylenediamine (>45°), a solid product is always obtained which contains 87% dilithium acetylide and 13% ethylenediamine. The ethylenediamine could not be removed with repeated washing; thus it must be attached chemically in some manner.

The basis for the reactions between hydrocarbons and amines with N-lithioethylenediamine depends on their relative acidities. In the absence of other effects, the most acidic hydrogen atom of the hydrocarbon or amine must be more acidic than the most acidic hydrogen on ethylenediamine to shift eq. 2 to the right. The

$$RH + NH_2CH_2CH_2NHLi \rightleftarrows RLi + NH_2CH_2CH_3NH_2 \quad (2)$$

pK_a values for several of the hydrocarbon and amines pertinent to this discussion have been published[3,4] recently and are reproduced in Table II.

TABLE II

ACIDITIES OF SELECTED HYDROCARBONS AND AMINES

Compd.	pK_a
Phenylacetylene	21
Indene	21
Diphenylamine	23
Fluorene	25
Aniline	27
Diphenylmethane	35
Ammonia	36
Toluene	37
Dimethyl sulfoxide	41

Our observations indicate that the pK_a value of ethylenediamine lies between 35 and 37 (*e.g.*, the order of magnitude of ammonia). N-Lithioethylenediamine does react slowly (but incompletely) with diphenylmethane producing the yellow color of diphenylmethyllithium in solution but does not react with toluene. An order of magnitude for this pK_a values was considered sufficient since such values are only good to one or two pK_a units under similar solvent conditions and can vary widely when measured in different solvents.[5]

Complex formation is also considered to be an important factor in the over-all reaction since eq. 3 is highly exothermic.

$$RLi + NH_2CH_2CH_2NH_2 \longrightarrow RLi\cdot NH_2CH_2CH_2NH_2 \quad (3)$$

Any ether or inert hydrocarbon can be used as solvent. However, dimethyl sulfoxide cannot be used as solvent since it is metalated by N-lithioethylenediamine. If N-lithioethylenediamine is dissolved in dimethyl sulfoxide and warmed and benzophenone added, an exothermic reaction takes place. Upon addition of large quantities of water, methylsulfinyldiphenylcarbinol[6] separates in quantitative yield. This is not surprising in light of the work of Ledwith and McFarlane[7] who report that the relative acidities of weak acids are meaningless when measured in dimethyl sulfoxide, since dimethyl sulfoxide is itself a weak acid.

The complexes may be prepared in a one-step process from lithium metal in hydrocarbon solvents, since the N-lithioethylenediamine can be prepared *in situ*. This offers obvious advantages in many cases.

Ethylenediamine, 1,2-diaminopropane, and 1,3-diaminopropane all form remarkably stable complexes with all of the lithiated amines and hydrocarbons studied. To illustrate this stability, N-lithio-N-methylaniline–ethylenediamine or indenyllithium–ethylenediamine when heated to reflux in toluene or xylene lost no ethylenediamine on attempted azeotropic distillation.[8] After cooling, each material was isolated unchanged.

With 1,4-diaminobutane the aromatic hydrocarbons fluorene and indene form fluorenyllithium–1,4-diaminobutane and indenyllithium–1,4-diaminobutane. On the other hand, the acetylenic hydrocarbons and amines did not form stable 1,4-diaminobutane complexes but formed the corresponding lithium acetylides and lithiated amines. 1,6-Diaminohexane behaves similarly.

Since acetylenic hydrocarbons and amines do not form stable complexes with 1,4-diaminobutane, they

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[2] Some of the products tend to separate as oils rather than crystalline solids. If the oil is seeded the product crystallizes exothermally. Seed crystals may generally be obtained by the slow addition of the corresponding amine or hydrocarbon to an ethereal slurry of N-lithioethylenediamine at −10° with vigorous stirring.

[3] M. Schlosser, *Angew. Chem., Intern. Ed. Engl.*, **3**, 287 (1964).

[4] D. J. Cram, *Chem. Eng. News*, **41**, No. 33, 92 (1963).

[5] Steiner and Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963).

[6] E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).

[7] A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964).

[8] The azeotropes involved are ethylenediamine–toluene (31.2:68.8 wt. %), b.p. 104° (752 mm.), and ethylenediamine–xylene (62.7:37.3 wt. %), b.p. 114° (758 mm.), as determined by the authors.

Table III

Reduction of Indene to Indane in the Preparation of Indenyllithium–Diamine in Toluene at Reflux

Diamine	Mole % of lithium entering into reduction
Ethylenediamine	19
1,4-Diaminobutane	9
1,6-Diaminohexane	0

Table IV

Reaction of Sodium, Ethylenediamine, and Hydrocarbons or Amines in Toluene at 35°

Hydrocarbon or amine	Na, g.-atom	Hydrocarbon or amine, mole	EDA, mole	Time, hr.	Recovered yield, %	Product
Acetylene	0.200	0.750	0.000	3	0	
Acetylene	0.200	0.250	0.020	1	98	$HC{\equiv}CNa$
Ethylacetylene	0.200	0.270	0.015	1	91	$CH_3CH_2C{\equiv}CNa$
Phenylacetylene	0.200	0.210	0.020	5	93	$C_6H_5C{\equiv}CNa$
Fluorene	0.200	0.200	0.020	4	10	$C_{13}H_9Na \cdot EDA$
Fluorene	0.200	0.200	0.200	4	87	$C_{13}H_9Na \cdot EDA$
Indene	0.200	0.200	0.020	4	10	$C_9H_7Na \cdot EDA$
Indene	0.200	0.200	0.200	4	84	$C_9H_7Na \cdot EDA$
Aniline	0.200	0.200	0.200	4	0	
N-Methylaniline	0.200	0.200	0.200	4	0	
Diphenylamine	0.200	0.200	0.200	4	0	

can be treated directly with lithium metal in the presence of 1,4-diaminobutane as a catalyst, according to the following reaction scheme. Using a 10:1 molar

$$Li + NH_2(CH_2)_4NH_2 \longrightarrow NH_2(CH_2)_4NHLi + 0.5H_2 \quad (4)$$

$$RH + NH_2(CH_2)_4NHLi \longrightarrow RLi + NH_2(CH_2)_4NH_2 \quad (5)$$

ratio of lithium–1,4-diaminobutane, lithium phenylacetylide was prepared in 88% recovered yield and N-lithiodiphenylamine in 86% recovered yield. Under similar conditions using 1,6-diaminohexane, lithium phenylacetylide was prepared in 93% recovered yield.

When using the one-step process, reduction of the hydrocarbons can compete with metalation because of the potentially reductive nature of a lithium–diamine system. Indeed, Bosch and Brown[9] have demonstrated that indene and fluorene can be reduced by lithium in dimethoxyethane.

If indene is present initially[10] in the preparation of indenyllithium–diamine complexes, varying amounts of reduction to indane can occur depending on the diamine employed (see Table III). Indene reduction can be avoided by preparing the lithiated diamine before introducing indene to the system.

Sodium powder reacts incompletely[11] with ethylenediamine under all conditions tested. Apparently N-sodioethylenediamine forms at the metal surface making it resistant to further attack by ethylenediamine. If, however, an appropriate RH compound is present to react with the formed N-sodioethylenediamine, fresh metal surface is exposed and over-all reaction will proceed to completion.

Fluorene and indene reacted with sodium and ethylenediamine in toluene at 35° to form fluorenylsodium–ethylenediamine and indenylsodium–ethylenediamine, respectively (see Table IV). Similar complexes were formed with 1,4-diaminobutane.

Acetylenic hydrocarbons reacted with sodium and ethylenediamine in toluene at 35° to form the corresponding sodium acetylide. Diamine complexes could not be obtained even on seeding with the corresponding lithium derivatives. It is possible that crystalline diamine complexes might form with sodium acetylenic hydrocarbons under proper conditions or there may be some steric reason for the instability of such complexes. Since diamine complexes are not formed, the diamines may be used in catalytic quantities.

Amines would not react with sodium and ethylenediamine under any conditions tested: toluene at 35°, toluene–tetrahydrofuran (50:50 vol. %) at 35°, or toluene at reflux.

Temperature is critical with sodium compounds. Below 30° the reaction rate is very slow, while above 40° softening of the sodium powder occurs resulting in agglomerations. If agglomerates form, further reaction is not practical.

Experimental

General.—The lithium metal powder was obtained by filtering a lithium dispersion (75 μ) in mineral oil, washing with hexane, and drying under argon. Sodium metal powder was prepared *in situ*.

All amines and hydrocarbons were used as obtained. Acetylene and ethylacetylene were purified by passage through columns containing activated alumina. Dimethyl sulfoxide was used as obtained. All other solvents were dried over sodium wire. All reactions were carried out under argon atmospheres.

Preparation of Indenyllithium–Ethylenediamine. From N-Lithioethylenediamine.—A 1-l., three-necked flask, equipped with a dropping funnel, condenser, high-speed stirrer, electric stirring motor, and thermometer, served as the reactor. A glass tee above the condenser served as a means for argon cover and as an exit for escaping gases.

N-Lithioethylenediamine (0.37 mole) was placed in the reactor and was followed by diethyl ether (370 ml.). Indene (0.38 mole) was added dropwise over a period of 1 hr. with stirring. Temperature was maintained at 25° with cooling for 3 hr. Hexane (370 ml.)[12] was then added. The resultant slurry was transferred under an argon atmosphere to a double-cone filter which had been thoroughly flushed with argon. Filtration was facilitated by a small argon pressure. The product was washed several times with hexane and dried by argon passage. The resultant pale green, free-flowing, crystalline solid was recovered in 95% yield.

The same general procedure was employed in all solvents. Gaseous reactants were introduced through gas addition tubes; solid reactants were dissolved in a minimum volume of solvent.

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(9) A. Bosch and R. K. Brown, *Can. J. Chem.*, **42**, 1718 (1964).

(10) In the absence of indene, 19 mole % of the lithium reduces toluene to methylcyclohexene.

(11) Depending on particle size of the sodium powder, 10–15% conversion.

(12) Recovered yields were about 10% lower if the hexane was not added, owing to partial solubility of the product in diethyl ether.

Preparation of Indenyllithium–Ethylenediamine. From Lithium Metal.—The apparatus was the same as that used above.

Lithium metal powder (0.37 g.-atom) was placed in the reactor and was followed by toluene (370 ml.). Ethylenediamine (0.37 mole) was added dropwise over a period of 20 min. with stirring. The temperature rose to reflux[13] during the addition and was maintained at reflux by heating for 30 min.

Indene (0.37 mole) was added over a 15-min. period. After an additional 15 min. the flask was cooled to room temperature. The resultant oil was crystallized by the addition of a seed crystal. The product was isolated as above in 95% recovered yield.

The same general procedure can be used with other hydrocarbons and diamines.

Preparation of Lithium Phenylacetylide Using Catalytic Quantities of 1,4-Diaminobutane.—The apparatus was the same as that used above.

Lithium metal powder (0.370 g.-atom), toluene (370 ml.), phenylacetylene (0.370 mole), and 1,4-diaminobutane (0.037 mole) were combined and heated at reflux for 4 hr. The resultant slurry was cooled to room temperature, filtered, washed with pentane, and dried under argon. The product was recovered in 88% yield.

Preparation of Sodium Phenylacetylide Using Catalytic Quantities of Ethylenediamine.—The apparatus was the same as above, except a 500-ml. flask was used.

Sodium metal (0.200 g.-atom) was dispersed in toluene (200 ml.). The slurry temperature was adjusted to 35° and ethylenediamine (0.020 mole) was added. Phenylacetylene (0.200 mole) was added over a 15-min. period (cooling to maintain 35°). The system was maintained at 35° for 5 hr. The product was recovered in 95% yield.

Analytical Procedures.—The analytical procedure was similar to that previously described.[1] Unreacted free metal was determined by measuring the hydrogen evolved from a hydrolyzed sample. Total lithium was determined spectrophotometrically. Diamines were determined as the difference between total basicity and total lithium.

Vapor phase chromatographic analyses were run isothermally on a silicone 200 column against known standards.

[13] In some cases initial reaction was sluggish. Warming aided initiation.

Small Charged Rings. VI. Expansion of the Aziridinium Ring by Reaction with Nitriles. A New Type of Benzylating Agent[1–3]

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The general (③$^+$ + ^{2} → ⑤$^+$) ring-expansion reaction of aziridinium salts has been extended to include reaction with nitriles, leading to formation of imidazolinium salts. Some N-alkyl-N-benzylimidazolinium salts have been found to undergo facile removal of the benzyl group and can serve as benzylating agents toward a variety of nucleophiles under acidic conditions.

We have extended the scope of the general[1,4] ③$^+$ + ^{2} → ⑤$^+$ ring-enlargement reaction of aziridinium salts to include synthesis of imidazolinium salts by interaction with nitriles[5] as weak nucleophiles. Postulated[1,4] for this general reaction is, as a first stage, the development of the more stable carbonium ion resulting from cleavage of the aziridinium ring, a β-3°-amino-3°-carbonium ion. At least two mechanistic pathways are available for the second stage of the reaction, which results in the formation of the five-membered ring (eq. 1). One possibility involves the intermediacy of a resonance-stabilized carbonium–oxonium ion in the case of aldehydes[4] and ketones[1] and a carbonium–nitrilium ion in the case of nitriles,[6] the subject of the present investigation. Attack of the nitrogen unshared pair of electrons on the carbonium ion center would complete the cyclization. The other major possibility is for an effective "1,3-polar cycloaddition" of the nucleophile to occur directly, with no semiattached intermediate detectable. Possible analogy may be found in the reaction of nitriles with azide anion[7] and with "1,3-dipolar" units such as hydrazoic acid,[8] alkyl azides,[9] diazoalkanes,[10] ketocarbenes,[11] azomethine imines,[12] nitrile imines,[13] nitrile oxides,[14] and nitrile ylides.[15]

When 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate (I), $C_{16}H_{24}ClNO_4$, was heated with excess acetonitrile a new substance, $C_{18}H_{27}ClN_2O_4$, was formed. Evidence that aziridinium ring expansion had taken place as expected[1,4] to give 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate (II) was seen in the infrared spectrum, where C═N stretching absorption appeared at 1715 cm.$^{-1}$. The high frequency was consistent with a neighboring positive charge. The structure assignment was also substantiated by the n.m.r. spectrum, in which signals were found for the imidazolinium methylene as an AB system of doublets at τ 6.13 and 6.55 and for the 2-

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[1] Paper V: N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *J. Org. Chem.*, **29**, 3383 (1964).

[2] This investigation was supported by a research grant (USPHS-GM-05829-06) from the National Institutes of Health, U. S. Public Health Service, to whom we are pleased to acknowledge our thanks.

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