

Table I. Absorption Maxima in Acetonitrile^c

Compd	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$	λ , Å	$10^{-4}\epsilon$
II	2860 (2820)	3.2 (2.9)								
III	3660 ^a (3650) ^a	0.9 ^b (4.8)	4255	1.0 ^b	4450	1.2 ^b	4565	1.3 ^b	6400 ^a (6300) ^a	0.5 ^b (2.8)
IV	4400 (4370)	6.2 (6.2)								

^a Dimer bands as discussed in text. ^b Relative molar absorptivities at 25° where the equilibrium constant, K , for the disproportionation process $II + IV \rightleftharpoons 2III$ has a value of 3.2×10^3 . ^c Parenthetical values are for *o*-T in aqueous solution, ref 1.

et al.,⁸⁻¹⁰ and others¹¹⁻¹³ for WB perchlorate. In 2:1 ethanol-ether solution, the hyperfine esr spectrum of I (the cation radical of *o*-T) was examined as a function of temperature. This dependence is shown in Figure 2. This behavior is also analogous to the WB perchlorate case as reported by Kawamori, *et al.*,¹⁴ and suggests a

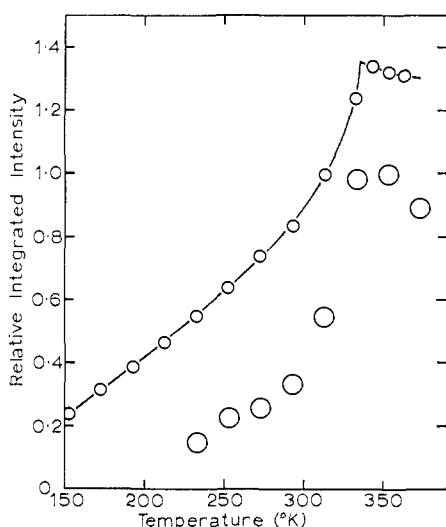


Figure 2. Temperature dependence of the integrated esr spectral intensities for $1.0 \times 10^{-4} M$ I in dry KCl (small circles) and $6 \times 10^{-4} M$ I in 2:1 ethanol-ether (large circles).

dimerization of the cation radical of *o*-T. Further evidence in support of this suggestion is provided by the concentration and temperature dependence of the visible spectrum of either I or electrogenerated *o*-T⁺ in both AN and ethanol-ether, the bands shown in Table I at 3660 and 6400 Å decreasing with both increasing temperature and decreasing concentration. The solution dimerization of *o*-T⁺ has also been observed in aqueous acidic medium, and a solid electrolysis product (presumably dimer) has also been noted.¹ The nature of the solution dimerization process is quite probably the formation of a charge-transfer complex.^{15,16}

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Assuming a dimerization mechanism, the temperature dependence of the integrated esr spectral intensities indicates that the enthalpy of the dissociation process is approximately 4 kcal mol⁻¹ for I both in solid KCl and in ethanol-ether solution.

The electropreparation and chemical and structural characterization of a series of these solid, stable, ionic free radicals are in progress.

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Synthesis of Aldehydes and Secondary Amines from Carboxylic Acids via Imines¹

Sir:

Burgstahler, Worden, and Lewis² have reported the reduction of carboxylic acids with lithium in ethylamine to a mixture of alcohols and aldehydes, the latter having been isolated in most cases as their 2,4-dinitrophenylhydrazone derivatives. They made no effort to develop this reaction as a general synthetic route to aldehydes. Since it has been shown in these laboratories that the reduction of carboxylic acids can be stopped cleanly at the aldehyde stage,³ it was felt that further investigation of the reaction for use as a synthetic method was warranted.

Multigram quantities of carboxylic acids were used and the aldehydes were isolated in pure form rather than as derivatives. Glpc of the reduction product showed that little if any alcohol was present. A significant result of the investigation was the identification of an imine⁴ formed during the product isolation

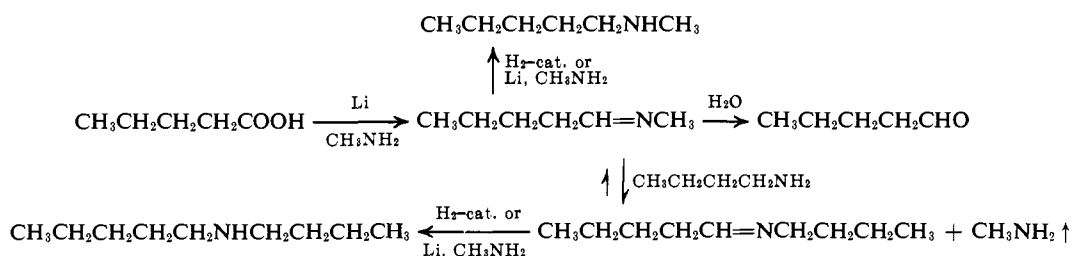
(1) (a) This work was supported in part by funds given to the University of Southern Mississippi by the Mississippi Board of Trustees of Institutions of Higher Education for the support of basic research. (b) Funds for the nmr spectrometer used in this investigation were provided by the National Science Foundation.

(2) (a) A. W. Burgstahler, L. R. Worden, and T. B. Lewis, *J. Org. Chem.*, **28**, 2918 (1963); (b) A. W. Burgstahler and L. R. Worden, *J. Amer. Chem. Soc.*, **83**, 2581 (1961); (c) *ibid.*, **86**, 96 (1964).

(3) This material was presented in part at the 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, and the 21st Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., Nov 1969.

(4) Imines had previously been isolated from lithium-methylamine reductions of furans in this laboratory (A. O. Bedenbaugh, J. H. Bedenbaugh, J. D. Aakins, and W. A. Bergin, *J. Org. Chem.*, **35**, 543 (1970)).

Scheme I



procedure used in the reduction of the acids. One reaction intermediate is thought to be a carbinolamine salt which is converted to the imine during the isolation procedure. The imine which is readily reduced to the corresponding amine cannot be present during the reduction since no amine is isolated. The imine (which can be isolated in good yield) is hydrolyzed to the aldehyde (slowly in neutral aqueous solution, rapidly in acidic aqueous solution), reduced to the corresponding amine (catalytically or with lithium in methylamine), and can undergo any other reaction of an imine. These conversions are illustrated using pentanoic acid as the starting material (Scheme I).

Because Burgstahler, Worden, and Lewis² acidified their product mixture, the imine which is rapidly hydrolyzed to the aldehyde was not noted by them. Basic aqueous solutions maintained during our work-up procedure enabled us to isolate the imine.

Saturated acids ranging from five to fourteen carbons (Table I), an unsaturated acid (8-octadecenoic), and a

Table I. Conversion of Carboxylic Acids to Aldehydes and *N*-Methylamines by Lithium in Methylamine

RCOOH	Yield, % ^a	
	RCHO	RCH ₂ NHCH ₃
CH ₃ (CH ₂) ₃ COOH	66	52
CH ₃ (CH ₂) ₆ COOH	59	
CH ₃ (CH ₂) ₈ COOH	61	68
CH ₃ (CH ₂) ₁₀ COOH	61	51
CH ₃ (CH ₂) ₁₂ COOH	84	51
(CH ₃) ₃ C(CH ₂) ₂ COOH	62	

^a The yields are of distilled product with no more than a 3° boiling range.

diacid (nonadioic⁵) were reduced with good results (yield ~60%). Use of the lithium-methylamine system converted *N*-(8-octadecenylidene)methylamine to the unsaturated compound, *N*-methyl-8-octadecenylamine, in 64% yield.

Reduction, in addition to that of the carboxyl group, was observed when compounds containing conjugated double bonds (C=CC=C, C=CCOOH, or ArCOOH) or nonconjugated double bonds separated by one methylene group (C=CCH₂C=C and C=CCH₂COOH) were subjected to lithium in methylamine.

When benzoic acid reacted with lithium in methylamine, reduction of the benzene ring as well as the

The imines obtained from this reduction contained considerably less condensation products than those prepared by Tiollais' method of combining aldehydes with methylamine (R. Tiollais, *Bull. Soc. Chim. Fr.*, 708 (1947); R. Tiollais and H. Guillermin, *C. R. Acad. Sci.*, 236, 1798 (1953)).

(5) Both carboxyl groups of the diacid were reduced because the lithium:acid ratio was 6:1 as compared with 3:1 used in monocarboxylic acids. Attempts to isolate aldehyde acids from the reduction mixture are currently in progress.

carboxyl group occurred. However, addition of ammonium nitrate to the reduction medium resulted in reduction of benzoic acid to benzaldehyde (~25%). This investigation involving the use of additives in the reduction is continuing.

The versatility of the reaction sequence in preparing secondary amines has been demonstrated in this laboratory by the conversion of *N*-pentylidenemethylamine *via* transimination with butylamine⁶ (Scheme I). The resulting imine can be reduced either catalytically or with the lithium-methylamine solution.

The reduction of pentanoic acid to pentanal has also been shown to occur by an electrolytic process using platinum electrodes, methylamine, and lithium chloride. Further studies of the electrolytic reduction of carboxylic acids in methylamine are being undertaken.

Reaction of pentanoic acid (25.2 g; 0.250 mol), methylamine (500 ml), and lithium wire (1.77 g; 0.255 g-atom) for 10–20 min resulted in a blue solution. If gelling occurred this could be eliminated by addition of more methylamine. An additional 3.43 g of lithium (0.495 g-atom) was then added. After 4.5 hr the reaction mixture was decomposed (250 ml of saturated aqueous NH₄Cl) and extracted with ether (best for aldehyde conversion) or pentane (best for amine conversion). A 66% yield of distilled pentanal was obtained by washing the ether extract consecutively with 10% hydrochloric acid (until the washings remained acidic), aqueous sodium bicarbonate solution, and water, and finally drying (Na₂SO₄). Alternately a 52% yield (see Table I) of distilled *N*-methylpentylamine was obtained after the pentane extracts were dried (Na₂SO₄), the solution concentrated (to 300 ml), and the imine reduced in a low-pressure Parr hydrogenation apparatus with 3.0 g of 10% Pd-C catalyst.

(6) The low boiling point of methylamine is one reason why it is preferable to ethylamine as the reaction medium.

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Negative-Ion Mass Spectrometry of Polynitroaromatics

Sir:

Numerous correlations have been established between positive ions found in the gas phase in the mass spectrometer and carbonium-ion intermediates in solution. By comparison, few correlations yet exist between carbanion or anion-radical solution chemistry and the gas-phase behavior of negative ions.