product was recrystallized from acetone giving 50.0 g. (71%) of white crystals, m.p. 108–110°.

Anal. Calcd. for $C_{12}H_{15}N_2O_2$: C, 66.05; H, 6.42; N, 12.84. Found: C, 66.67; H, 6.43; N, 12.78.

1-Phenyl-2-methyl-2-hydrazinopropane hydrochloride (VIII). Fifty grams (0.22 mole) of *N*-2-phenyl-*t*-butylsydnone was treated with 100 cc. of concd. hydrochloric acid and heated on a steam bath for 15 min. It was cooled on an ice bath and saturated with dry hydrogen chloride. The solid was removed by filtration and the process was repeated twice. The product was recrystallized from absolute methanol and ether giving 10.0 g. (22%) of white crystals—m.p. 139–141°.

Anal. Calcd. for $C_{10}H_{17}N_2Cl$: C, 59.85; H, 8.47; N, 13.96; Cl, 17.70. Found: C, 59.11; H, 8.49; N, 14.12; Cl, 17.62.

N-(1-Phenyl-2-t-butyl)-N^1-isopropylhydrazine hydrochloride (XI). 1-Phenyl-2-methyl-2-hydrazinopropane, 1.2 g. (0.007 mole), and 0.4 g. (0.006 mole) of acetone were mixed and allowed to stand at room temperature for 5 hr. The turbid solution was dissolved in ether, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residual oil was dissolved in 25 cc. of absolute ethanol and hydrogenated using platinum dioxide as the catalyst at 60 lbs. pressure. The hydrogenation was completed in 1 hr. It was filtered, cooled on an ice bath and saturated with dry hydrogen chloride. The solvent was removed *in vacuo* and the solid was recrystallized from absolute methanol and ether giving 0.5 g. (28%) of white crystals, m.p. 143–145°.

Anal. Calcd. for $C_{13}H_{13}N_2Cl$: C, 64.32; H, 9.48; N, 11.54; Cl, 14.63. Found: C, 64.61; H, 9.59; N, 11.50; Cl, 14.60.

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Chemistry of Aryl Isocyanates. The Influence of Metal Carboxylates on the Aryl Isocyanate–Ethyl Carbanilate Reaction

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In previous work it was shown that, at elevated temperature, aryl isocyanates and substituted ethyl carbanilates react slowly,[1,2] to form an equilibrium mixture of the starting materials and ethyl α,γ-diarylallophanate. It has now been found that metal carboxylates will catalyze this reaction at room temperature to give ethyl α,γ-diarylallophanate, Table I, in good yield. The yield of product is dependent upon the metal carboxylate and, as the data in Table I show, lead and cobalt carboxylates are the best catalysts for this reaction.

The use of these metal derivatives was extended to substituted aryl isocyanates and carbanilates to form substituted diarylallophanates (I).

$$\mathrm{R{-}C_6H_4NH}\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{N(C_6H_4R')COOR''}$$

(I)

where
R = H, *o*-CH_3, *p*-Cl, *p*-CH_3
R′ = H, *p*-CH_3, *m*-OCH_3
R″ = C_2H_5, C_6H_5

The reaction does not proceed when ethyl carbanilate or phenyl isocyanate are replaced by ethyl carbamate or ethyl isocyanate respectively.

At room temperature the metal carboxylates except the zinc derivative slowly catalyze the formation of triphenyl isocyanurate from phenyl isocyanate. Lead and cobalt derivatives are the most active catalysts. To verify that trimerization of phenyl isocyanate is considerably slower than allophanate formation when lead or cobalt carboxylates are used as catalysts, equimolar quantities of phenyl isocyanate and ethyl carbanilate were reacted at room temperature in the presence of a small quantity of cobalt 2-ethylhexanoate. A 95.5% yield of ethyl α,γ-diphenylallophanate and 0.84% of triphenyl isocyanurate was obtained.

EXPERIMENTAL[3]

Preparation of ethyl α,γ-diphenylallophanate. To a solution consisting of 11.9 g. (0.1 mole) of phenyl isocyanate and 16.5 g. (0.1 mole) of ethyl carbanilate was added 0.15 g. of cobalt 2-ethylhexanoate in mineral spirits. After 6 hr. the purple reaction mixture solidified. To the solid was added 100 ml. of hot petroleum ether (b.p. 30–60°) and the solution filtered rapidly. A white crystalline product weighing 0.1 g. (0.84%) and melting at 277–278° was obtained. A mixture melting point with an authentic sample of triphenyl isocyanurate, m.p. 278°, gave no depression. The filtrate was then evaporated to dryness and the residue recrystallized from ethyl alcohol. There was obtained a white crystalline solid weighing 27.1 g. (95.5%), m.p. 92–94°. A mixture melting point with an authentic sample of ethyl α,γ-diphenylallophanate, m.p. 94° gave no depression, m.p. 92–94° The following compounds were prepared in a similar manner using cobalt 2-ethylhexanoate in mineral spirits.

Ethyl-α,o-methoxyphenyl-γ-phenylallophanate, yield (51%), m.p. 95°. The infrared spectrum exhibited a twin carbonyl band at 5.92 and 5.94 μ.

Anal. Calcd. for $C_{17}H_{18}N_2O_4$: N, 8.6. Found: 8.9.

Ethyl-α,p-chlorophenyl-γ,p-tolylallophanate, yield (66%), m.p. 96°. The infrared spectrum exhibited a twin carbonyl band at 5.82 and 5.95 μ.

Anal. Calcd. for $C_{17}H_{17}N_2O_3Cl$: N, 8.4 Found: 8.5.

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(1) I. C. Kogon, *J. Am. Chem. Soc.*, 78, 4911 (1956).

(2) I. C. Kogon, *J. Org. Chem.*, 24, 83 (1959).

(3) All melting points were determined in a Fischer-Herschberg apparatus and are uncorrected.

TABLE I

Allophanate Formation Catalyzed by Metal Carboxylates at Room Temperature[a,b]

$C_6H_5NCO + C_6H_5NHCOOC_2H_5 \longrightarrow C_6H_5NHCON(C_6H_5)COOC_2H_5$

No.	Metal Carboxylate	Concentration of Metal, Mole/L. × 10⁵	Time, Hr.	Yield of Allophanate, %
1	Lead naphthenate	7.7	4	96
2	Cobalt naphthenate	6.1	6	96
3	Copper naphthenate	11.2	88	69
4	Manganese naphthenate	6.0	88	69
5	Iron naphthenate	6.9	88	36
6	Cadmium naphthenate	6.0	88	10
7	Vanadium naphthenate	5.5	88	10
8	Lead 2-ethylhexanoate	5.2	5	95
9	Zinc 2-ethylhexanoate	5.2	5	95
10	Manganese 2-ethylhexanoate	7.1	88	10
11	Cobalt 2-ethylhexanoate	6.2	7	97
12	Lead linoresinate	5.4	5	96
13	Cobalt linoresinate	6.1	7	96
14	Manganese linoresinate	7.3	88	45
15	Zinc linoresinate	10.1	88	12
16	Copper linoresinate	12.2	88	50
17	Iron linoresinate	5.2	90	42

[a] The catalysts were supplied by the Harshaw Chemical Co. as mineral spirits solutions. [b] The reaction was carried out by allowing a mixture of 1.05 g. (0.0088 mole) of phenyl isocyanate, 1.48 g. (0.009 mole) of ethyl carbanilate and catalyst to stand at room temperature. The reaction mixture was then worked up in the manner described in the experimental section.

Ethyl-α,o-chlorophenyl-γ,m-methoxyphenylallophanate, yield (75%), m.p. 106°. The infrared spectrum exhibited a twin carbonyl band at 5.83 and 5.96 μ.

Anal. Calcd. for $C_{17}H_{17}N_2O_4Cl$: N, 8.1. Found: 8.1.

Ethyl-α,γ-di-p-tolylallophanate, yield (76.6%), m.p. 104–106°. The infrared spectrum exhibited a twin carbonyl band at 5.73 and 5.88 μ.

Anal. Calcd. for $C_{18}H_{20}N_2O_3$: N, 9.0 Found: 9.1.

Phenyl-α,γ-diphenylallophanate, yield (75%), m.p. 139–141°. The infrared spectrum exhibited a twin carbonyl band at 5.75 and 5.85 μ.

Anal. Calcd. for $C_{20}H_{16}N_2O_3$: N, 8.5. Found: 8.8.

Infrared absorption spectrum. Infrared absorption spectra were determined with a Perkin-Elmer Infrared Spectrophotometer Model No. 21. No solvent was used. The spectra were determined as Nujol mulls in a demountable cell using sodium chloride windows with 0.025-mm. spaces (normal thickness).

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2,2-Dinitroethylamine and Derivatives

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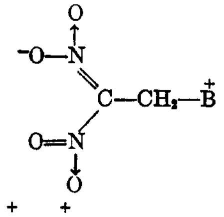
Zeldin and Shechter[1] have described the formation of 2-guanidino-1,1-dinitroethane (Ia), 1,1-dinitro-2-piperidinoethane (Ib) and trimethylammonium N-(2-nitroethyl-2-nitronate) (Ic) in the reaction of 1,1,1-trinitroethane with the corresponding free bases. Ultraviolet spectra, solubility behavior, and crystalline form lent strong support to the characterization of these compounds as zwitterionic salts.[2] We wish now to record the syntheses and some novel reactions of two additional members of this class of compounds, 2,2-dinitroethylamine (II) and *N*,*N*-dimethyl-2,2-dinitroethylamine (III).



Ia. $\overset{+}{B} = \overset{+}{N}H{=}C(NH_2)_2$

Ib. $\overset{+}{B} = \overset{+}{N}HC_5H_{10}$ (piperidino)

Ic. $\overset{+}{B} = \overset{+}{N}(CH_3)_3$

II. $\overset{+}{B} = \overset{+}{N}H_3$

III. $\overset{+}{B} = \overset{+}{N}H(CH_3)_2$

The reaction of 1,1,1-trinitroethane with methanolic ammonia at room temperature proceeded smoothly with only a mild exotherm to yield II (85%), the by-product ammonium nitrite decomposing under the conditions of the reaction to nitrogen and water. With dimethylamine in aqueous methanol the yield of the *N*,*N*-dimethyl derivative III was 65%. The products in both instances were only slightly soluble and precipitated directly from the reaction mixture sufficiently pure for elemental analyses. Since excess base increased the

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(1) L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, 79, 4708 (1957).

(2) For simplicity of nomenclature, however, these compounds are named as if they were in the nonionic form except where this becomes too cumbersome as with Ic.