

The aqueous phase was acidified and extracted with ether. Evaporation of the ether left no weighable quantity of the *cis*-*exo* acid.

**Reaction of Acetylphenylacetylene (III) with Cyclopentadiene.**—Ten grams of III<sup>11</sup> and 50 g. of cyclopentadiene in 75 ml. of *m*-xylene were refluxed for 36 hr. The solvents were distilled under reduced pressure. Distillation of the residue gave 11.6 g. (79%) of 2-acetyl-3-phenyl-2,5-norbornadiene (XV), b.p. 86–93° (0.08–0.1 mm.);  $\lambda_{\text{max}}^{\text{neat}}$  3.28 (sh), 3.35, 6.08, 7.37, 7.74, 8.11, 13.20, 13.81, 14.28  $\mu$ . The 2,4-dinitrophenylhydrazone was prepared as red crystals from ethyl acetate–ethanol, m.p. 164–165°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub>: C, 64.61; H, 4.65; N, 14.35. Found: C, 64.55; H, 4.54; N, 14.27.

**3-Phenyl-2,5-norbornadiene-2-carboxylic Acid (XVI).**—To a cooled solution of 10 g. (0.25 mole) of sodium hydroxide and 1.5 ml. (0.0275 mole) of bromine in 50 ml. of water was added 1.1 g. (0.0053 mole) of XV in 35 ml. of dioxane. After stirring at 0° for 10 hr., the excess sodium hypobromite was destroyed by addition of sodium bisulfite. Extraction with ether, drying of the ethereal extract over magnesium sulfate, and concentration of the solution *in vacuo* gave 0.98 g. (89%) of XVI. Recrystallization from ether–petroleum ether gave white crystals, m.p. 135–136°; lit.<sup>4,12</sup> m.p. 135–136°.

**endo-2-Acetyl-endo-3-phenylnorbornane (XIII). I. From X.**—A suspension of 0.1 g. of 10% palladium on charcoal, 0.60 g. of X, and 25 ml. of benzene was hydrogenated at 40 p.s.i. for 4 hr. Filtration of the catalyst and removal of the solvent left a light yellow oil,  $\lambda_{\text{max}}^{\text{neat}}$  3.31 (sh), 3.40, 5.91, 6.28, 13.36, 14.25  $\mu$ ;  $n_{\text{D}}^{20}$  1.5543.

**II. From XV.**—A suspension of 1.0 g. of 10% palladium on charcoal in 40 ml. of methanol was stirred in an atmosphere of hydrogen until uptake was negligible. A solution of 5.5 g. of XV in 50 ml. of methanol was added and the mixture was allowed to take up hydrogen until uptake ceased. Filtration of the catalyst and removal of the solvent gave a theoretical yield of XIII,  $n_{\text{D}}^{20}$  1.5547. The infrared spectrum of this sample was identical with that obtained from reduction of X. The 2,4-dinitrophenylhydrazone prepared in the normal way was an oil. Crystallization was obtained by using the same procedure as for the 2,4-dinitrophenylhydrazone of X, m.p. 110–111°. Two further recrystallizations from ethyl acetate–ethanol gave the pure derivative, m.p. 115–116°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>: C, 63.95; H, 5.62; N, 14.20. Found: C, 64.01, H, 5.80; N, 14.11.

**endo-3-Phenylnorbornane-*exo*-2-carboxylic Acid (XIV).**—A 0.20-g. portion of XIII in 15 ml. of dioxane was added to a cooled solution of 4 g. (0.1 mole) of sodium hydroxide and 0.75 ml. (0.0185 mole) of bromine in 20 ml. of water. The solution was stirred at 0° for 4 hr., then at room temperature for 30 hr. Sodium bisulfite was added to reduce the excess hypobromite. Acidification with dilute hydrochloric acid, extraction with ether, drying over magnesium sulfate, and concentration of the ethereal solution gave a crystalline residue. Recrystallization from ethanol–water gave white crystals, m.p. 109–118°. A second recrystallization from ether–petroleum ether (90–120°) gave XIV, m.p. 138–139°; lit.<sup>2</sup> m.p. 139°. This compound showed no depression in melting point when mixed with an authentic sample.<sup>17</sup>

## The Synthesis and Reactions of N,N'-Dicarbalkoxy-N,N'-dialkoxyhydrazines and Some Observations on Carbalkoxyium Ions

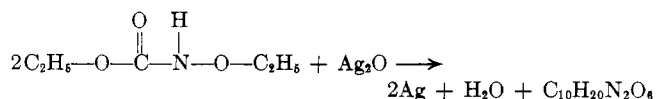
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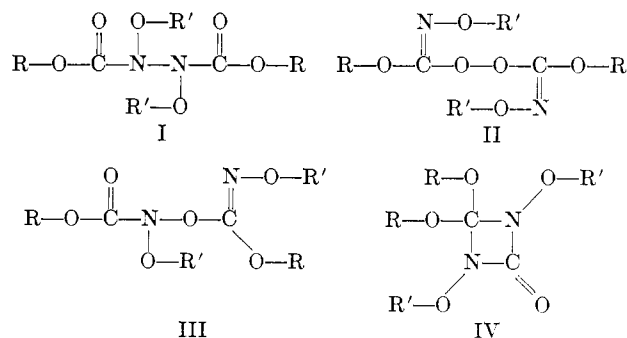
N-Carbalkoxy-O-alkylhydroxylamines react readily with silver oxide in diethyl ether to give N,N'-dicarbalkoxy-N,N'-dialkoxyhydrazines in almost quantitative yields. These hydrazines are very sensitive towards strong acids and bases and do not undergo the normal type of ester hydrolysis. The products from the decomposition with *p*-toluenesulfonic acid in diethyl ether and 1-propanol provided evidence for the formation of carbonium ions and carbalkoxyium ions. A new type of mixed anhydride, carbomethoxy *p*-toluenesulfonate, is reported.

Attempts to alkylate N-carbomethoxy-O-ethylhydroxylamine<sup>2</sup> with ethyl iodide in the presence of silver oxide led to the discovery of an interesting coupling reaction, which proceeded equally well in the absence of ethyl iodide.<sup>3</sup>



The product, isolated in a 91% yield, was found to have a molecular weight of 261 and to fit the empirical formula C<sub>10</sub>H<sub>20</sub>N<sub>2</sub>O<sub>6</sub> (mol. wt., 264). The infrared spectrum of the compound displayed strong absorption at 1750 cm.<sup>-1</sup> and the absence of any absorption above 3000 cm.<sup>-1</sup> dismissed the possibility of any NH or OH groups. The compound's n.m.r. spectrum showed two methylene quartets (at 5.76 and 5.95  $\tau$ ) of equal intensity and two methyl triplets (at 8.67 and 8.77  $\tau$ ) also of

equal intensity. From the ratios of the peaks, methylene to methyl ratio was 2:3, the n.m.r. spectrum indicated the presence of two different ethoxy groups. Assuming a minimum of rearrangements the three structures anticipated for the material are I to III.



Structure II is essentially a peroxide and it is not expected to absorb above 1700 cm.<sup>-1</sup> for the carbon–nitrogen double bond.<sup>4</sup> The compound was stable on distillation at 110° (0.7 mm.) and did not give the products that one would expect from II upon hydrolysis.

(4) The infrared spectrum of (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>C=N–OCH<sub>3</sub> shows an intense band at 1646 cm.<sup>-1</sup>; unpublished work of R. Raap.

(1) Holder of a Province of Alberta Graduate Fellowship, 1962–1963.

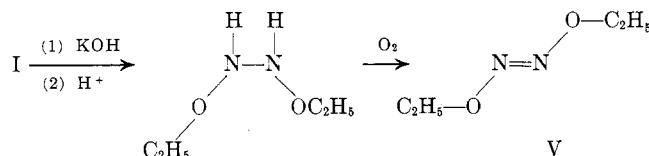
(2) We have chosen to name these compounds as derivatives of hydroxylamine, because of the ambiguity and redundancy of the previously used names, e.g., O-ethylcarbomethoxyhydroxamic acid and  $\alpha$ -ethylhydroxyurethane.

(3) The silver salt of N-carbomethoxy-O-benzylhydroxylamine was isolable and was converted to the coupling product at room temperature in ether, thus indicating that the silver salt is indeed an intermediate in the reaction.

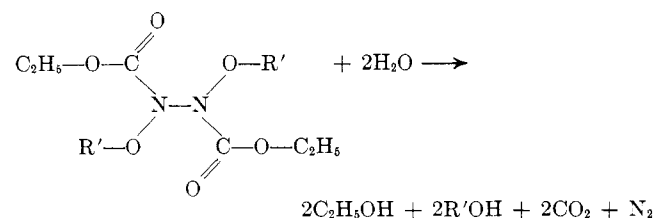
TABLE I  
N,N'-DICARBALKOXY-N,N'-DIALKOXYHYDRAZINES PREPARED BY  
SILVER OXIDE OXIDATION

R	R''	Yield %	B.p., °C. (mm.)	$\nu_{\text{C=O}}$ in $\text{cm.}^{-1}$	$n_D^{25}$
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	91	107-108 (0.7)	1750	1.4331
Ia C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	97	...	1750	1.5198
Ib <i>i</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>2</sub> H <sub>5</sub>	94	106-107 (0.3)	1748	1.4339
Ic CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	84	93-94 (0.6)	1755	1.4360
Id C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	94	95-96 (0.5)	1755	1.4352
Ie C <sub>2</sub> H <sub>5</sub>	CH <sub>2</sub> =CH-CH <sub>2</sub>	80	119-120 (0.8)	1750	1.4527

Structure III was dismissed on the basis of its n.m.r. spectrum which contained only two different ethoxy groups, and the infrared spectrum of the compound displayed only one maximum in the double bond region, whereas III would be expected to show two maxima. Structure IV could fit all the spectral data, but seems unlikely considering its origin and the hydrolysis products. It was thus considered very probable that the compound has structure I, in which the carbonyl absorption is expected to be much like that of the starting material (*i.e.*, 1750  $\text{cm.}^{-1}$  in the product compared with 1730  $\text{cm.}^{-1}$  in the reactant). Thus, it seemed probable that hydrolysis followed by oxidation would convert I to the known diethyl hyponitrite (V).<sup>5</sup>



Although compound I could be refluxed in a methanol-water mixture without noticeable decomposition, the addition of acidic or basic substances resulted in an immediate evolution of gas. Decomposition of I at 0° in methanol with an excess of potassium hydroxide yielded one equivalent of nitrogen. Approximately three equivalents (2.7 and 2.9 equiv. on two separate experiments) of gas, a 2:1 mixture of carbon dioxide and nitrogen, was evolved when a methanolic solution of I was added dropwise to a refluxing solution of methanol and aqueous hydrochloric acid. Benzyl alcohol, in an approximately 90% yield, could be isolated from the reaction between compound Ia and methanolic potassium hydroxide or hydrochloric acid. Thus the stoichiometry for the acid-catalyzed hydrolysis may be expressed as shown.

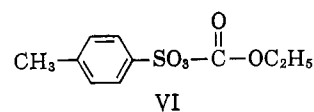


The formation of nitrogen gas and rapidity of the decarboxylation process indicated that the analogous mechanism for the decarboxylation of azoformic esters to diimide was not operative here. This removed any hope of converting I into the known hyponitrite ester

(5) J. R. Partington and C. C. Shah, *J. Chem. Soc.*, 2589 (1932).

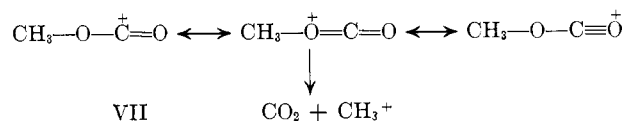
and suggested that the reaction should be examined more carefully.

To this end we carried out the acid-catalyzed decomposition of I in anhydrous diethyl ether and in the presence of hydroxylic solvents. The high boiling material, obtained from the reaction of I and *p*-toluenesulfonic acid (either the monohydrate or the anhydrous material) in ethereal solution, was found to be a mixture of ethyl *p*-toluenesulfonate and another compound which had a n.m.r. spectrum similar to ethyl *p*-toluenesulfonate but which absorbed intensely at 1780  $\text{cm.}^{-1}$  in the infrared. The ethyl *p*-toluenesulfonate could be isolated either by distillation or by elution chromatography over alumina in a 22% yield.<sup>6</sup> All attempts to purify the carbonyl containing compound by elution chromatography over alumina (acid, basic, and neutral grade) or silica gel resulted in decomposition with gas evolution on the column. However, additional information proved the structure to be carbethoxy *p*-toluenesulfonate (VI) (see next paragraph). The reaction mixture of I and *p*-toluenesulfonic acid also contained a small amount of diethyl carbonate.<sup>7,8</sup> Control experi-



ments demonstrated that carbethoxy *p*-toluenesulfonate does not decompose under the reaction conditions into ethyl *p*-toluenesulfonate, and neither does diethyl carbonate arise from a reaction between the ethanol, formed in the reaction, and carbethoxy *p*-toluenesulfonate.

The formation of the two *p*-toluenesulfonates suggests that the corresponding carbonium ions are generated during the reaction and that acyl nitrogen cleavage is occurring rather than acyl oxygen cleavage as would be expected from ester hydrolysis.<sup>9</sup> In order to test this assumption, the reactions of anhydrous *p*-toluenesulfonic acid with N,N'-dicarbalkoxy-N,N'-diethoxyhydrazine (Ib) and N,N'-dicarbomethoxy-N,N'-diethoxyhydrazine (Ic) were investigated. If the reaction does produce alkyl carbonium ions, then Ib would be expected to give *t*-butyl *p*-toluenesulfonate and some *sec*-butyl *p*-toluenesulfonate, whereas Ic could be expected to give rise to a much higher yield of the carbomethoxy *p*-toluenesulfonate if the carbomethoxylium<sup>10</sup> ion VII is the precursor to the methyl carbonium ion.



The infrared spectrum of the products of the reaction of Ib with anhydrous *p*-toluenesulfonic acid in ether showed a strong band at 1778  $\text{cm.}^{-1}$  due to carbisobutoxy *p*-toluenesulfonate, and a smaller band at 1735

(6) The per cent yield in such cases is based upon two ethyl groups in I being able to give this product.

(7) Decomposition of I with dry hydrogen chloride in ether leads to ethyl chloroformate (25%), nitrogen, and some diethyl carbonate.

(8) The yield of duplicate runs being 10 and 12% as measured by g.l.p.c. using an internal standard.

(9) M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

(10) The name carbalkoxylium ion is used in a generic sense and may be applied to any alkyl group, *i.e.*, carbomethoxylium ion, in a manner analogous to the dimethylcarbamylium ion (see ref. 15).

cm.<sup>-1</sup> ascribed to isobutyl ethyl carbonate (no attempt was made to isolate this compound). The n.m.r. spectrum of the products, after the removal under vacuum of any low boiling components, indicated that the main product was carbisobutoxy *p*-toluenesulfonate, but by comparison with the n.m.r. spectra of authentic iso- and *sec*-butyl *p*-toluenesulfonate it could be shown that no isobutyl *p*-toluenesulfonate was present and that a small amount of *sec*-butyl *p*-toluenesulfonate was present in the reaction mixture<sup>11</sup> as indicated by a sextet centered at 5.49  $\tau$ .

The reaction with Ic produced methyl *p*-toluenesulfonate and carbomethoxy *p*-toluenesulfonate in an approximate ratio of 1:9 as indicated by the n.m.r. spectrum of the solid obtained by removing the low boiling material.<sup>12</sup> The solid could be recrystallized from a hexane-benzene solution and carbomethoxy *p*-toluenesulfonate was obtained in pure form in a 38% yield. Carbomethoxy *p*-toluenesulfonate is a white solid, melting at 60-61°, and has a strong band in its infrared spectrum at 1782 cm.<sup>-1</sup>. The compound on storing for ten weeks at room temperature was converted into methyl *p*-toluenesulfonate to the extent of approximately 80%. When carbomethoxy *p*-toluenesulfonate was allowed to react with a solution of aniline in ether, there resulted a 93% yield of N-carbomethoxy aniline and a 98% yield of anilinium *p*-toluenesulfonate. We have been unable to find any examples of this type of mixed anhydride in the literature.

Additional insight into the decomposition of N,N'-dicarbalkoxy-N,N'-dialkoxyhydrazines by strong acid was obtained by carrying out the decomposition in a manifold excess of alcohol. Table II reports the yields of the products formed from the decomposition of I and Ic in 1-propanol.

TABLE II

PRODUCTS FROM THE DECOMPOSITION OF N,N'-DICARBOMETHOXY-N,N'-DIETHOXYHYDRAZINE (Ic) AND N,N'-DICARBOMETHOXY-N,N'-DIETHOXYHYDRAZINE (I) IN 1-PROPANOL AT ROOM TEMPERATURE

Products <sup>a</sup>	Ic. <sup>b</sup> %	I. %
<i>n</i> -C <sub>3</sub> H <sub>7</sub> -O-R	11.1, 11.3	26.6, 27.1
<i>n</i> -C <sub>3</sub> H <sub>7</sub> -O-CO <sub>2</sub> R	56.3, 56.1	34.0, 32.0
C <sub>2</sub> H <sub>5</sub> -O-CO <sub>2</sub> R	14.0, 14.2	8.2, 8.2
Average total	81	68

<sup>a</sup> The products were determined by g.l.p.c. using toluene as an internal standard on a two-meter Ucon LB-550-X column.

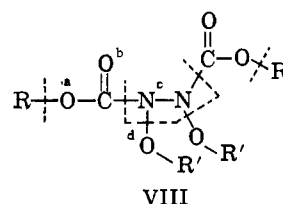
<sup>b</sup> See ref. 6.

### Discussion

The results described allow certain mechanistic interpretations. The occurrence of ethers in the acid-catalyzed hydrolysis of compounds I and Ic in alcohol (Table II) is verification of the formation of carbonium ions under these mild conditions. Four different sites of protonation are possible in these molecules. Sites a and c may be eliminated on the basis of the products that would be expected from the decomposition of the conjugate acid. The high yields of nitrogen and alcohols, R'OH, along with the formation of carbon dioxide in aqueous medium indicates that cleavage of the bonds

(11) Any *t*-butyl *p*-toluenesulfonate formed during the reaction must have decomposed as no indication of its presence was observed. See H. M. Hoffman, *Chem. Ind.*, 336 (1963).

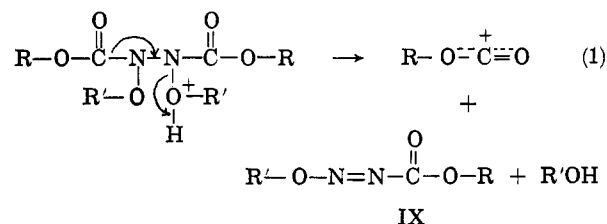
(12) The proportions of ethyl *p*-toluenesulfonate and carbomethoxy *p*-toluenesulfonate obtained under similar conditions was approximately 3:5.



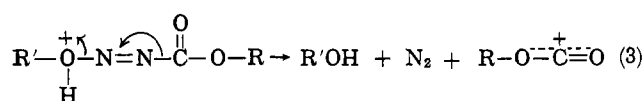
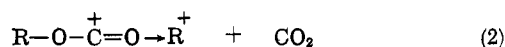
VIII

indicated by dotted lines in VIII is required to explain the products. Protonation at d (Scheme A) leads conveniently to all of the products, and changing the alkyl groups produced the anticipated change of product proportions.

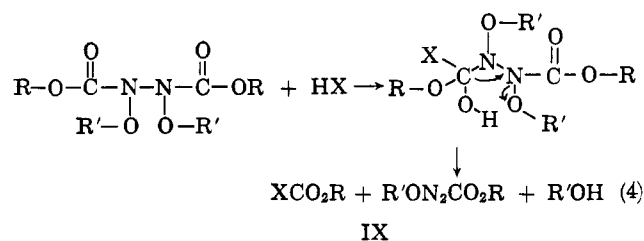
SCHEME A



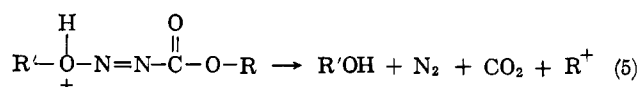
IX



SCHEME B



IX

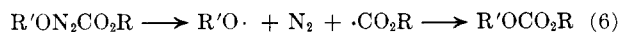


Scheme B seems unlikely inasmuch as it implies the formation of an adduct of *p*-toluenesulfonic acid to the carbonyl group. The addition mechanism also would predict the formation of dipropyl carbonate by ester interchange<sup>9</sup> of I with 1-propanol in the reaction of I with acid in 1-propanol. An attempt to observe any dipropyl carbonate by g.l.p.c. (Table II) led to the conclusion that it was not present in a detectable amount (*i.e.*, less than 0.1%). That the postulated intermediate IX may be the sole source of the alkyl carbonium ions, by equation 5, cannot be ruled out. It is, however, evident that the intermediate IX must also give rise to the carbomethoxylium ion since the n.m.r. spectrum of the solid residue from the reaction of Ic with an excess of anhydrous *p*-toluenesulfonic acid in ether indicated that the yield, before purification, of carbomethoxy *p*-toluenesulfonate was 60% (see also Table II). It seems likely, however, that the decomposition of VII into the alkyl carbonium ion (reaction 2) would be facile. The carbalkoxylium ion has been suggested as an intermediate in the solvolysis of alkyl chloroformates<sup>13</sup> and appears to be a plausible inter-

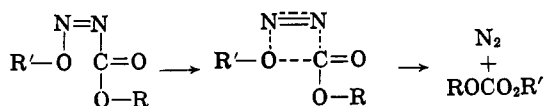
(13) M. Green and R. F. Hudson, *J. Chem. Soc.*, 1076 (1962), and previous work cited therein.

mediate in the decomposition of alkyl chloroformates<sup>14</sup> to alkylhalides. Hall<sup>15</sup> has observed a similar ion, XII, in the solvolysis of *N,N*-dimethylcarbamoyl chloride.

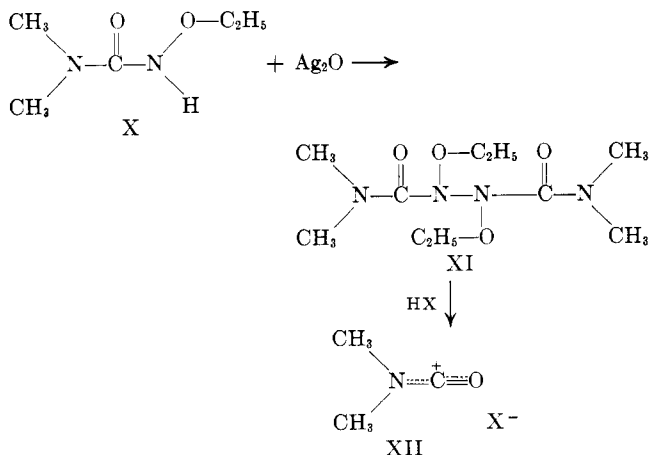
Attempts to trap the intermediate IX with cyclopentadiene were fruitless, as were all attempts to observe an ultraviolet spectrum attributable to IX. It seems likely that IX is hydrolyzed as rapidly as it is formed in view of the stability of the products formed upon hydrolysis (equation 3 and/or 5). Due to the amount of methyl ethyl carbonate and diethyl carbonate formed when I and Ic were decomposed in 1-propanol (Table II) it seemed possible that a homolytic pathway such as reaction 6 was responsible for the elusiveness of the postulated intermediate. All attempts to trap, by the use of cumene, any radicals



formed failed to give any bicumyl.<sup>16</sup> These carbonates are believed to be formed simply by virtue of the carbalkoxylium ion's reactivity and, even though the 1-propanol is in manifold excess, the alcohol, R'OH, generated contiguous to the carbonium ion reacts in the manner of an ion-neutral molecule pair.<sup>17</sup> The possibility also exists that the azo intermediate IX could decompose *via* a molecular four-center mechanism similar to that proposed by Huisgen and Krause<sup>18</sup> for the rearrangement of *N*-nitroso acetanilide into the metastable diazoacetate. This would require a *syn*-geometry for IX, and seems less likely than the following mechanism.



An attempt was made to prepare *N,N'*-bis(dimethylcarbamoyl)*N,N'*-diethoxyhydrazine (XI) by the silver oxide oxidation of *N*-dimethylcarbamoyl-*O*-ethylhydroxylamine (X). This, upon acid hydrolysis, would



(14) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, **77**, 2774 (1955). Although these authors suggest that the alkyl chloroformates decompose through the ion pair  $R^+ \cdot O_2CCl^-$ , there is no definitive evidence to decide between it and the ion pair  $ROCO^+ \cdot Cl^-$ .

(15) H. K. Hall, Jr., *ibid.*, **77**, 5993 (1955).

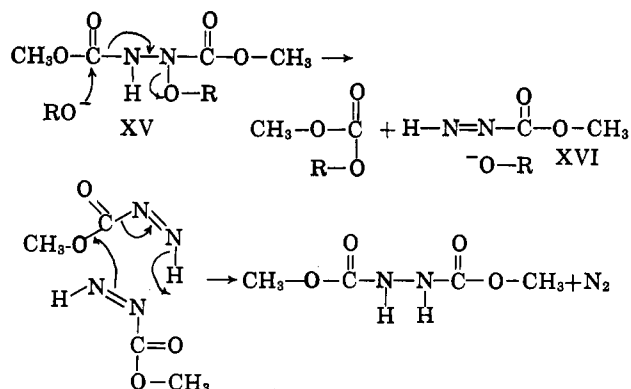
(16) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962). These authors found the carbo-*t*-butoxy radical to be scavengable with cumene at 25° from the decomposition of di-*t*-butyl monoperoxyoxalate.

(17) The ion-neutral molecule pair has also been referred to as an "encumbered carbonium ion." R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **82**, 4730 (1960).

(18) R. Huisgen and L. Krause, *Ann.*, **574**, 157 (1951).

be expected to lead to the carbonium ion XII, which has previously been observed by Hall.<sup>15</sup> It was thus hoped that salt-like structures would have been observed. The only products that could be isolated from the silver oxide oxidation of X were *N,N'*-bis(dimethylcarbamoyl)hydrazine (XIII) and the corresponding azo compound XIV.<sup>19</sup>

The mode of reaction of these compounds enables us to propose a mechanism for the reaction of *N,N'*-dicarbomethoxy-*N*-alkoxyhydrazines (XV) and methanol observed by Diels and Wulff.<sup>20</sup> The decomposition in alcohol was catalyzed by a potassium acetate crystal to produce one mole of dialkyl carbonate and one-half mole of nitrogen and hydrazo formic ester per mole of reactant.



Further attempts to trap IX and XVI are now in progress.

## Experimental

The infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer equipped with grating optics. Nuclear magnetic resonance spectra were measured using a Varian Associates Model A-60 spectrometer, with tetramethylsilane as a reference. Vapor phase chromatography was carried out with a Perkin-Elmer Model 154 vapor fractometer. A 2-m. column packed with Ucon LB-550-X was used. In those instances where absolute amounts of reaction products were determined, an accurately known amount of either cyclohexane or toluene as internal standard was added to the reaction mixture. The relationship between the ratio of peak areas of the products with their absolute weight ratios was obtained by comparing the chromatograms with authentic mixtures of approximately the same composition as the product mixtures.

The microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, West Germany.

***N,N'*-Dicarbomethoxy-*N,N'*-diethoxyhydrazine (I).**—A mixture of *N*-carbomethoxy-*O*-ethylhydroxylamine<sup>21</sup> (62.0 g., 0.46 mole) and silver oxide (70.0 g., 0.30 mole) in 150 ml. of ether was allowed to reflux for 2 hr., after which silver and excess silver oxide were filtered off and filtrate was dried over anhydrous magnesium sulfate. The colorless residue obtained after evaporation of the ether was distilled *in vacuo* to give 56 g. (91%) of a pale yellow oil boiling at 106–107° (0.7 mm.);  $n_D^{25}$  1.4331.

*Anal.* Calcd. for  $C_{10}H_{20}N_2O_6$ : C, 45.44; H, 7.63; N, 10.63; mol. wt., 264.3. Found: C, 45.66; H, 7.58; N, 10.75; mol. wt. by isothermal distillation,<sup>22</sup> 261.5.

**Silver Salt of Benzyl Carbomethoxyhydroxamate.**—To a solution of *N*-carbomethoxy-*O*-benzylhydroxylamine<sup>23</sup> (8.6 g., 44.6 mmoles)

(19) The n.m.r. spectrum of X in deuteriochloroform shows a single signal at 7.08  $\tau$  as does XIII at 7.03  $\tau$  (in  $D_2O$ ), whereas XIV (in  $CDCl_3$ ) displays restricted rotation of the methyl groups and a doublet at 6.82 and 6.92  $\tau$ . See M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

(20) O. Diels and C. Wulff, *Ann.*, **437**, 309 (1924).

(21) L. W. Jones, *Am. Chem. J.*, **20**, 40 (1898).

(22) E. P. Clark, *Anal. Chem.*, **13**, 820 (1941).

(23) B. J. R. Nicolaus, G. Pagani, and E. Testa, *Helv. Chim. Acta*, **45**, 1381 (1962).

and potassium hydroxide (2.50 g., 44.6 mmoles) in 100 ml. of 50% aqueous ethanol, cooled in ice, was slowly added, with vigorous stirring, a solution of silver nitrate (7.80 g., 45.8 mmoles) in 20 ml. of water. The gray solid which precipitated was washed with ethanol and anhydrous ether and kept for 16 hr. in a vacuum desiccator over phosphorus pentoxide in the dark. The precipitate amounted to 11.2 g. (90%), which upon heating underwent a vigorous decomposition into a black solid at 101–102°.

**N,N'-Dicarbethoxy-N,N'-dibenzoxyhydrazine (Ia).**—A solution of N-carbethoxy-O-benzylhydroxylamine<sup>23</sup> (10.0 g., 51.5 mmoles) and silver oxide (8.0 g., 34.5 mmoles) were refluxed in 50 ml. of ether for 24 hr. The solution was filtered and washed three times with a concentrated sodium bisulfite solution to remove some benzaldehyde that was formed in the reaction. The ether solution was dried over magnesium sulfate, and the ether was evaporated. The residue (8.0 g., 81%,  $n_D^{25}$  1.5205) still contained a small amount of benzaldehyde (about 2%).

A much purer product (as indicated by n.m.r. spectroscopy) was obtained from the silver salt of N-carbethoxy-O-benzylhydroxylamine. This silver salt (11.0 g.) was suspended in 50 ml. of anhydrous ether and stirred for 18 hr. at room temperature. Evaporation of the ether, after the silver was filtered off, produced 6.8 g. (97%) of residue; an n.m.r. spectrum of the oil indicated that only Ia was present;  $n_D^{25}$  1.5198.

*Anal.* Calcd. for  $C_{20}H_{24}N_2O_6$ : C, 61.84; H, 6.23. Found: C, 61.51; H, 6.40.

**N,N'-Dicarbisobutoxy-N,N'-diethoxyhydrazine (Ib).**—N-Carbisobutoxy-O-ethylhydroxylamine was prepared by the method of Jones<sup>21</sup>; b.p. 59–60° (0.4 mm.);  $n_D^{25}$  1.4275. A solution of N-carbisobutoxy-O-ethylhydroxylamine (10.5 g., 65.2 mmoles) and silver oxide (9.0 g., 38.8 mmoles) in 40 ml. of anhydrous ether was refluxed for 2 hr., filtered, dried, and the ether removed. The residue was distilled *in vacuo*; yield, 9.8 g. (94%); b.p. 106–107° (0.3 mm.);  $n_D^{25}$  1.4339.

*Anal.* Calcd. for  $C_{14}H_{20}N_2O_6$ : C, 52.48; H, 8.81; N, 8.75. Found: C, 52.49; H, 8.95; N, 9.19.

**N-Carbomethoxy-O-ethylhydroxylamine.**—Carbomethoxyhydroxamic acid<sup>24</sup> (45 g., 0.50 mole) was dissolved in 350 ml. of ethanol containing potassium hydroxide (28 g., 0.50 mole). Ethyl iodide (78.0 g., 0.50 mole) was added and the solution refluxed for 2 hr. The potassium iodide was filtered off and the ethanol evaporated, and the residual oil was taken up with ether. The ether layer was then extracted four times with 50-ml. portions of 20% sodium hydroxide. The aqueous layer was acidified with concentrated hydrochloric acid and saturated with sodium chloride. It was then extracted with six 50-ml. portions of ether. The combined ether layers were washed with a small amount of sodium thiosulfate solution and the residue obtained, after drying over magnesium sulfate and evaporation of the ether, was distilled *in vacuo* to yield 27.4 g. (46%), of product; b.p. 56–57° (2.0 mm.);  $n_D^{25}$  1.4246.

The n.m.r. spectrum of the product showed a quartet  $-CH_2-O-$  at 6.15  $\tau$ , a singlet  $-O-CH_3$  at 6.30  $\tau$ , a triplet at 8.78  $\tau$  due to  $-C-CH_3$ , and a broad peak at 1.8  $\tau$  due to NH. The relative areas were 2:3:3:1, respectively.

**N,N'-Dicarbomethoxy-N,N'-diethoxyhydrazine (Ic).**—A solution of N-carbomethoxy-O-ethylhydroxylamine (27.2 g., 22.9 mmoles) in 75 ml. of anhydrous ether, was allowed to react with silver oxide (31.0 g., 13.3 mmoles) for 1.5 hr. at 25°. The solution was filtered, dried, the ether evaporated, and the residual oil distilled to give 22.5 g. (84%) of a pale yellow oil; b.p. 93–94° (0.6 mm.);  $n_D^{25}$  1.4360.

*Anal.* Calcd. for  $C_8H_{16}N_2O_6$ : C, 40.67; H, 6.83; N, 11.86. Found: C, 40.93; H, 6.81; N, 12.11.

**N,N'-Dicarbethoxy-N,N'-dimethoxyhydrazine (Id).**—A solution of N-carbethoxy-O-methylhydroxylamine<sup>21</sup> (25.5 g., 0.214 mole) and silver oxide (30.5 g., 0.131 mole) in 50 ml. of ether was placed in a flask fitted with a reflux condenser. A smooth exothermic reaction caused the ether to reflux for about 30 min., after which stirring was continued for an additional 45 min. The solid residue was filtered off and the filtrate dried over magnesium sulfate. The colorless residue obtained after evaporation of the ether was distilled *in vacuo*; yield, 23.8 g. (94%); b.p. 95–96° (0.5 mm.);  $n_D^{25}$  1.4352.

*Anal.* Calcd. for  $C_8H_{16}N_2O_6$ : C, 40.67; H, 6.83; N, 11.86. Found: C, 40.53; H, 6.83; N, 11.98.

**N,N'-Dicarbethoxy-N,N'-dialloxyhydrazine (Ie).**—A solu-

tion of N-carbethoxy-O-allylhydroxylamine<sup>25</sup> (8.35 g., 57.6 moles) and silver oxide (10.0 g., 43.1 mmoles) in 30 ml. of anhydrous ether was refluxed for 1.5 hr., after which it was filtered, dried, and the ether evaporated. The colorless residue was distilled *in vacuo* to give 6.30 g. (80%) of product, b.p. 119–120° (0.8 mm.);  $n_D^{25}$  1.4527. This compound decomposes slowly at room temperature, which may account for the low carbon analysis.

*Anal.* Calcd. for  $C_{12}H_{20}N_2O_6$ : C, 49.99; H, 6.99; N, 9.72. Found: C, 48.72; H, 6.70; N, 10.16.

**N-Dimethylcarbamoyl-O-ethylhydroxylamine (X).**—A saturated aqueous solution of O-ethylhydroxylamine hydrochloride (20 g., 0.20 mole) was treated with enough of a concentrated sodium hydroxide solution just to neutralize the acid. The solution was then extracted several times with ether. The ether solution (100 ml.) was dried over magnesium sulfate, filtered, and triethylamine (20.5 g., 0.203 mole) and dimethylcarbamoyl chloride (20.5 g., 0.191 mole) were added. The mixture was stirred at room temperature for an hour, the triethylamine hydrochloride filtered off, and the ether evaporated. The product was precipitated by adding hexane. Dimethylcarbamoyl chloride (5.5 g., 0.051 mole) was recovered from the filtrate. The N-dimethylcarbamoyl-O-ethylhydroxylamine was twice recrystallized from a 1:1 mixture of *n*-hexane and benzene; yield, 8.5 g. (47%, based on unrecovered dimethylcarbamoyl chloride); m.p. 79–80°.

*Anal.* Calcd. for  $C_5H_{12}N_2O_2$ : C, 45.43; H, 9.15; N, 21.19. Found: C, 45.19; H, 9.06; N, 21.04.

**Reaction of N-Dimethylcarbamoyl-O-ethylhydroxylamine with Silver Oxide.**—N-Dimethylcarbamoyl-O-ethylhydroxylamine (5.0 g., 22 mmoles) was dissolved in 40 ml. of methylene chloride and silver oxide (5.0 g., 22 mmoles) and magnesium sulfate (4.0 g.) were added. The reaction was initiated by heating, after which no further heat had to be applied and the exothermic reaction continued for about 10 min. causing the solvent to reflux. The mixture was refluxed an additional half hour, the solid filtered off, and an intense orange colored filtrate was obtained. The addition of ether caused a white solid (m.p. 217–218°) to precipitate. A mixture melting point with authentic N,N'-bis(dimethylcarbamoyl)hydrazine showed no depression; m.p. 219–220°. Their infrared spectra were superimposable; yield, 0.29 g. (10%).

The filtrate was evaporated, leaving a dark oily residue with the peppermint like odor of ethyl N,N-dimethylcarbamate. The residue partially solidified and the solid was recrystallized from a benzene-hexane (1:5) mixture, giving 0.5 g. of a yellow solid. This solid was purified by elution chromatography to give a bright yellow product, m.p. 111–112°, which by comparison (melting point, mixture melting point, and infrared spectrum) proved to be identical with an authentic sample of tetramethylazoforamide.

**N,N'-Bis(dimethylcarbamoyl)hydrazine.**—A solution of triethylamine (19.0 g., 0.188 mole), 95% hydrazine (3.0 g., 0.090 mmole), and dimethylcarbamoyl chloride (20.0 g., 0.186 mole) in 150 ml. of methylene chloride was refluxed for 5 hr. The reaction mixture was cooled, the triethylamine hydrochloride and the desired product precipitated, and filtered. The solid was dissolved in 300 ml. of absolute ethanol and washed with three 15-ml. portions of a saturated potassium carbonate solution. The ethanol solution was dried with sodium sulfate and concentrated under reduced pressure to a volume of about 100 ml. The N,N'-bis(dimethylcarbamoyl)hydrazine was precipitated by adding 200 ml. of acetone. Recrystallization of the product from 250 ml. of ethanol-ethyl acetate (1:1) produced 7.2 g. (46%) of white needles, m.p. 220–221°.

*Anal.* Calcd. for  $C_6H_{14}N_4O_2$ : C, 41.36; H, 8.10; N, 32.16. Found: C, 41.45; H, 8.06; N, 32.43.

**N,N,N',N'-Tetramethylazoforamide (XIV).**—A solution of N,N'-bis(dimethylcarbamoyl)hydrazine (1.0 g., 5.7 mmoles) in 40 ml. of methanol was shaken with silver oxide (1.3 g., 5.6 mmoles) for a few minutes. The solution turned orange very rapidly with the concomitant formation of silver. The solution was dried with sulfate and filtered. Removal of methanol under reduced pressure yielded 0.95 g. of a yellow solid, which was recrystallized from *n*-hexane-benzene (5:1) solution producing 0.8 g. (81%) of long yellow needles, m.p. 112–113°.

*Anal.* Calcd. for  $C_6H_{12}N_4O_2$ : C, 41.85; H, 7.02; N, 32.54. Found: C, 41.60; H, 7.12; N, 32.50.

(24) L. W. Jones and R. Oesper, *J. Am. Chem. Soc.*, **36**, 2208 (1914).

(25) R. F. Kleinschmidt and A. C. Cope, *ibid.*, **66**, 1929 (1944).

**Reaction of N,N'-Dicarboalkoxy-N,N'-dialkoxyhydrazines with Acid and Base. With Potassium Hydroxide.**—N,N'-Dicarbethoxy-N,N'-dimethoxyhydrazine (Id) (0.603 g., 9.74 mmoles) in 20 ml. of methanol was added dropwise to a solution of potassium hydroxide (5.0 g.) in methanol, at 0°. The gas that was evolved was passed through two U-shaped tubes, the first one filled with potassium hydroxide pellets, the second cooled in Dry Ice acetone. The volume of gas was measured with a gas buret and converted to STP. Calcd. for one equivalent per mole, 57 ml. Found, 56 ml.

The mass spectrum of the gas indicated it to be only nitrogen.

**B. With Hydrochloric Acid.**—Approximately 0.4 g. of I in 10 ml. of methanol was slowly added to a refluxing solution of 20 ml. of methanol and 5 ml. of 37% hydrochloric acid. The gas evolved was measured and converted to STP giving 67 and 77 ml. of gas from 0.291 g. and 0.317 g. of I, respectively. Calcd. for three equivalents per mole, 74 and 80 ml. The gas was shown to be a 2:1 mixture of carbon dioxide and nitrogen by mass spectrometric analysis.

**Reaction of Ia with Potassium Hydroxide.**—A sample of Ia (0.85 g.) was hydrolyzed with potassium hydroxide in methanol, and the benzyl alcohol was isolated, 0.39 g. (83%), by ether extraction.

A 1.0-g. sample of Ia in 20 ml. of methanol was allowed to react with 37% aqueous hydrochloric acid, and the work-up produced 0.51 g. (93%) of benzyl alcohol.

**Reaction of I with Anhydrous *p*-Toluenesulfonic Acid in Ether.**—In several experiments 1–2 g. of I was dissolved in approximately 20 ml. of anhydrous ether and to this solution was slowly added an excess of anhydrous *p*-toluenesulfonic acid in 50 ml. of ether. The reaction mixture was allowed to reflux, after which the ether solution was washed with two 20-ml. portions of 10% sodium bicarbonate and dried over anhydrous sodium sulfate. Most of the ether was then distilled. The absolute amount of diethyl carbonate (10–12%) was determined by g.l.p.c. using cyclohexane as an internal standard. When all the volatile materials were removed *in vacuo*, a mixture of ethyl *p*-toluenesulfonate and carbethoxy *p*-toluenesulfonate (in an approximate proportion of 3:5, respectively, as indicated by n.m.r. spectroscopy) was left behind. Several attempts were made to separate these materials. Carbethoxy *p*-toluenesulfonate decomposes on basic, acid, and neutral washed alumina. Silica gel failed to effect a separation. The residue displayed an infrared spectrum very similar to that of ethyl *p*-toluenesulfonate except for an intense peak at 1780  $\text{cm}^{-1}$ , and other additional peaks in the 1200- to 1000- $\text{cm}^{-1}$  region. Upon distillation of the residue the carbonyl containing compound was decomposed and the product (approximately 22%) was identical with ethyl *p*-toluenesulfonate, b.p. 117–118° (0.7 mm.).

**Control Experiment on the Products of the Reaction of I with Anhydrous *p*-Toluenesulfonic Acid in Ether.**—Anhydrous *p*-toluenesulfonic acid (4.0 g., 23.3 mmoles) in 55 ml. of anhydrous ether was added dropwise to a solution of N,N'-dicarbethoxy-N,N'-diethoxyhydrazine (1.54 g., 5.8 mmoles) in 20 ml. of ether in 1 hr. The ether solution was washed twice with 10% aqueous sodium bicarbonate and dried. The ether was distilled and the volatile materials were removed *in vacuo* at 70°. A mixture, A, of ethyl *p*-toluenesulfonate and carbethoxy *p*-toluenesulfonate (1.53 g.) was obtained. Part of this mixture (1.37 g.) was refluxed for 16 hr. with *p*-toluenesulfonic acid (2.0 g., 11.7 mmoles) and absolute ethanol (2.0 g., 43.5 mmoles) in 50 ml. of anhydrous ether. After the work-up, as described, a residue was obtained. An infrared spectrum of the residue showed that no diethyl carbonate was formed *via* a reaction between carbethoxy *p*-toluenesulfonate and ethanol. All the volatile material was then removed *in vacuo* at 70° and mixture B (1.22 g.) was obtained. The infrared and n.m.r. spectra of mixtures A and B were identical, indicating that no ethyl *p*-toluenesulfonate results from carbethoxy *p*-toluenesulfonate under these conditions.

**Carbomethoxy *p*-Toluenesulfonate.**—N,N'-Dicarbomethoxy-N,N'-diethoxyhydrazine (Ic) (4.00 g., 16.9 mmoles) was dissolved in 20 ml. of anhydrous ether. A solution of anhydrous *p*-

toluenesulfonic acid (6.0 g., 34.9 mmoles) in 50 ml. of ether was added dropwise in 1 hr. The exothermic reaction maintained the ether at the reflux temperature. The ether was washed with two 20-ml. portions of 10% aqueous sodium bicarbonate and dried over magnesium sulfate. The ether was then distilled and the residue was held *in vacuo* at 60° for 10 min. to remove all volatile materials. The yield of residue was 5.01 g., which solidified slowly at room temperature. An n.m.r. spectrum of the solid showed that the ratio of carbomethoxy *p*-toluenesulfonate to methyl *p*-toluenesulfonate was 9:1. The solid was purified by dissolving it at room temperature in a mixture of 30 ml. of *n*-hexane and 15 ml. of benzene and cooling. The white needles were filtered off yielding 2.90 g. (38%), m.p. 54–57°. Three subsequent recrystallizations raised the melting point to 60–61°.

*Anal.* Calcd. for  $\text{C}_9\text{H}_{10}\text{O}_6\text{S}$ : C, 46.95; H, 4.37; S, 13.92. Found: C 46.89; H, 4.47; S, 14.35.

**Reaction of N,N'-Dicarbisoobutoxy N,N'-Diethoxy Hydrazine (Ib) with Anhydrous *p*-Toluenesulfonic Acid in Ether.**—A solution of *p*-toluenesulfonic acid (4.4 g., 25.5 mmoles) in 50 ml. of anhydrous ether was added dropwise to a refluxing solution of the hydrazine (2.04 g., 6.4 mmoles) in 20 ml. of ether. The reaction mixture was washed with two 20-ml. portions of 10% aqueous sodium bicarbonate and then dried over magnesium sulfate. After the ether was evaporated and all volatile materials were removed *in vacuo* at room temperature, there remained 1.73 g. of high boiling liquid residue, the infrared spectrum of which showed strong carbonyl absorption at 1780  $\text{cm}^{-1}$  and weak absorption at 1740  $\text{cm}^{-1}$ . The n.m.r. spectrum showed the absence of isobutyl *p*-toluenesulfonate (no methylene doublet at 6.27  $\tau$ ). Instead it showed a strong doublet at 6.09  $\tau$  which was ascribed to carbisoobutoxy *p*-toluenesulfonate. The sextet

of the H-C-O in *sec*-butyl *p*-toluenesulfonate at 5.49  $\tau$  was present

although the signal was weak; this signal became more pronounced when part of the carbisoobutoxy *p*-toluenesulfonate was decomposed with alumina. The carbisoobutoxy *p*-toluenesulfonate could not be isolated in pure form.

**Decomposition of I and Ic in 1-Propanol by a Catalytic Amount of *p*-Toluenesulfonic Acid.**—An accurately known amount (about 1 g.) of I (or Ic) was dissolved in 15 ml. of predistilled reagent grade 1-propanol, in a 50-ml. round bottom flask equipped with a reflux condenser. A small amount of anhydrous *p*-toluenesulfonic acid was added. The reaction was allowed to proceed at room temperature for 18–24 hr. until the gas evolution had ceased. During the course of the reaction a catalytic amount of acid was added two to three times. The propyl ether and dialkyl carbonates were determined quantitatively by g.l.p.c., using toluene as an internal standard. The results are summarized in Table II.

**Reaction of Carbomethoxy *p*-Toluenesulfonate with Aniline.**—A solution of aniline (0.40 g., 4.3 mmoles) in 10 ml. of anhydrous ether was added to carbomethoxy *p*-toluenesulfonate (0.40 g., 1.7 mmoles) in 10 ml. of anhydrous ether. A white precipitate formed immediately. The precipitate was filtered off and amounted to 0.45 g. (98%) of *N*-phenyl ammonium *p*-toluenesulfonate, identified by its infrared spectrum. The filtrate was washed twice with 20-ml. portions of 4% aqueous hydrochloric acid, dried, and the ether evaporated. The oily residue was left *in vacuo* for 2 hr., after which it solidified upon cooling to give 0.23 g. (92%), m.p. 46–48°, of *N*-carbomethoxyaniline. A mixture melting point with an authentic sample showed no depression, and the infrared spectra were superimposable.

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