within 2% of the theoretical volume calculated from the weight of triphenylsilane. Pseudo-first-order rate constants were calculated from the usual plots of log (V_∞ − V) against time and they agreed, within experimental error, with rate constants obtained using the more conventional apparatus described in an earlier paper.[5] The results are shown in Table II.
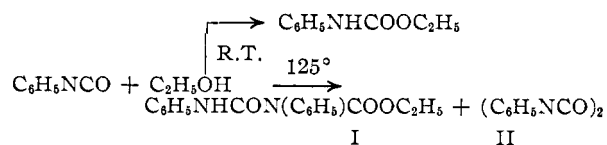

New Reactions of Phenyl Isocyanate and Ethyl Alcohol[1]

BY I. C. KOGON

Phenyl isocyanate reacts with ethyl alcohol at 125° to give a 22.9% yield of ethyl α,γ-diphenylallophanate and a trace of phenyl isocyanate dimer. When N-methylmorpholine is added as a catalyst, the reaction is altered and the product is triphenylisocyanurate (isocyanate trimer) in excellent yield. Phenyl isocyanate without the ethyl alcohol and heated under the same conditions in the presence of N-methylmorpholine yields only a small quantity of phenyl isocyanate dimer. Evidence is presented supporting ethyl α,γ-diphenylallophanate and phenyl isocyanate dimer as intermediates that lead to the formation of triphenylisocyanurate.

It has been known for many years that ethyl carbanilate is formed when phenyl isocyanate reacts with ethyl alcohol at room temperature.[2] We have now found that when the temperature is elevated to 125° the product is ethyl α,γ-diphenylallophanate (I) and a small quantity of phenyl isocyanate dimer II.[3]

$$C_6H_5NCO + C_2H_5OH \xrightarrow[\substack{R.T.\\125°}]{\longrightarrow C_6H_5NHCOOC_2H_5}$$

$$C_6H_5NHCON(C_6H_5)COOC_2H_5 + (C_6H_5NCO)_2$$
$$\qquad\qquad I \qquad\qquad\qquad\qquad II$$

Lakra and Dains[4] carried out a similar reaction at 150°, but they did not isolate I; their only product was a small quantity of carbanilide. The formation of the carbanilide was probably due to traces of moisture present in the reaction mixture.

Ethyl carbanilate also reacts with phenyl isocyanate to give I and II and is probably an intermediate for this reaction. In order to understand further this reaction a study was made of the effect of substituents on the reactivity of ethyl carbanilate and phenyl isocyanate (Table I). Electron-donating groups in the aromatic ring of the carbanilate and electron-withdrawing groups in phenyl isocyanate appeared to aid the reaction. An unexpected result was the relatively high yield of product obtained when phenyl isocyanate was treated with ethyl p-chlorocarbanilate.

When N-methylmorpholine (NMM) was used as a catalyst for the reaction of phenyl isocyanate and ethyl alcohol, the reaction was altered and triphenylisocyanurate (III) was obtained in excellent

(1) Presented before the section on Organic Chemistry, Eighth Annual Delaware Chemical Symposium at Newark, Delaware, February 1956.

(2) (a) R. L. Shriner and R. C. Fuson, "Identification of Pure Organic Compounds," 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136; (b) C. Naegali, A. Tyaliji, L. Conrad and F. Litwan, *Helv. Chim. Acta*, **21**, 1100, 1127 (1938); (c) D. S. Tarbell, R. C. Mallatt and J. W. Wilson, THIS JOURNAL, **64**, 2229 (1942); (d) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

(3) A. W. Hofmann, *Ber.*, **4**, 247 (1871). The infrared spectrum and melting point of I were identical with those of the product obtained from Hofmann's procedure.

(4) H. Lakra and F. B. Dains, THIS JOURNAL, **51**, 2220 (1929).

yield. Ethyl alcohol could again be replaced by ethyl carbanilate to give the same product.

$$C_6H_5NCO + C_2H_5OH \xrightarrow[125°]{NMM}$$

$$+ \, C_6H_5NHCOOC_2H_5$$
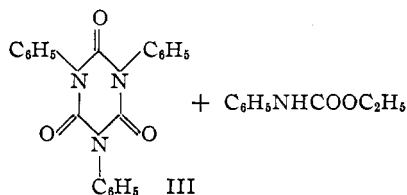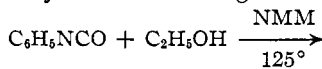
The reaction was extended to include substituted aromatic isocyanates and substituted ethyl carbanilates. The results are summarized in Table II. In order to demonstrate that only the initial aryl isocyanate and none of the carbanilate enters into the formation of triarylisocyanurate, the following mixtures were heated in the presence of a catalytic quantity of NMM: (a) phenyl isocyanate and ethyl p-chlorocarbanilate, (b) p-tolyl isocyanate and ethyl carbanilate, (c) o-chlorophenyl isocyanate and ethyl m-chlorocarbanilate. The major product isolated in each case was the triarylisocyanurate of the initial aryl isocyanate present. The yield of product from these reactions was lower than the yield of product from the experiments in which the aryl isocyanate and the substituted ethyl carbanilates had the same substitution on the aromatic ring. This lower yield from reactions a, b and c is probably due to an exchange reaction between the aryl isocyanate and the substituted ethyl carbanilate.[5] No trimeric product was isolated from a mixture of phenyl isocyanate, ethyl N-methyl carbanilate and NMM heated at 125° for 24 hours. The hydrogen atom present on the nitrogen of ethyl carbanilate therefore must be important in the formation of III. Phenyl isocyanate gives III when heated with a small quantity of a basic inorganic salt.[6-9] We have trimerized a number of aryl iso-

(5) E. J. Goldberg, private communication.

(6) A. W. Hofmann, *Ber.*, **3**, 765 (1870); **4**, 246 (1871).

(7) W. Trentzel, *ibid.*, **21**, 411 (1888).

(8) J. Blair and G. Smith, THIS JOURNAL, **56**, 907 (1934).

(9) H. Staudinger, "Die Ketene," Enke, Stuttgart, 1912, pp. 126-127.

TABLE I
ALKYL α,γ-DIARYLALLOPHANATES

Compound	Temp., °C.	Time, hr.	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Found
$C_6H_5NHCON(C_6H_5)COOC_2H_5$	140	24	22.9	92–94[a]		
$C_6H_5NHCON(p\text{-}CH_3C_6H_4)COOCH_3$	120	24	60.0	124–125[b]	9.8[d]	9.7
$C_6H_5NHCON(p\text{-}CH_3OC_6H_5)COOC_2H_5$	125	24	65.0	136–137[c]	8.9	9.4
$C_6H_5NHCON(p\text{-}ClC_6H_5)COOC_2H_5$	125	24	45.2	89–90[c]	8.8	8.7
$o\text{-}NO_2C_6H_5NHCON(C_6H_5)COOC_2H_5$	125	20	19.0	116–118[c]	12.8	13.2
$p\text{-}CH_3OC_6H_5NHCO(C_6H_5)COOC_2H_5$	125	20	3.3	116–118[c]	8.9	8.8
$p\text{-}CH_3OC_6H_5NHCO(p\text{-}CH_3OC_6H_5)COOC_2H_5$	125	20	73.2	130–131[c]	8.1	8.3

[a] Recrystallized from carbon tetrachloride–petroleum ether. [b] Recrystallized from hot water. [c] Recrystallized from ethyl alcohol. [d] *Anal.* Calcd. for $C_{17}H_{18}N_2O_3$: C, 67.6; H, 5.6. Found: C, 67.9; H, 5.6.

TABLE II
1,3,5-TRIARYLISOCYANURATES

Aryl group	Time, hr.	Yield, %	M.p., °C.	Carbon Calcd.	Found	Hydrogen Calcd.	Found	Nitrogen Calcd.	Found
Phenyl	25	98.8	280[a]					11.7	11.6
p-Tolyl	3	87.6	264	72.1	72.2	5.2	5.3	10.5	10.4
p-Nitrophenyl	1	80.0	350	57.2	57.3	2.4	2.0	17.1	17.2
p-Methoxyphenyl	7	81.0	260	64.3	64.0	4.7	4.8	9.4	9.4
p-Chlorophenyl	2.5	75.0	318					9.2[b]	9.1
o-Tolyl	20	85.0	180					9.4	9.5
o-Nitrophenyl	1	82.0	260					17.1	17.8
o-Methoxyphenyl	20	85.0	261					9.4	9.2
o-Chlorophenyl	10	86.0	201	54.7	54.2	2.6	3.1	9.1	9.2

[a] All the triarylisocyanurates were recrystallized from ethyl alcohol. [b] *Anal.* Calcd. for $C_{21}H_{12}N_3O_3Cl_3$: Cl; 23.1. Found: Cl, 23.1.

cyanates by this method. It is also well known that catalysts such as triethylphosphine and pyridine lead to the dimerization of phenyl isocyanate.[10-12] We have now found that NMM is also a catalyst for the dimerization of phenyl isocyanate. This reaction is reversible.[13]

On the basis of the present study we propose that the trimerization of phenyl isocyanate in the presence of ethyl alcohol or ethyl carbanilate and NMM proceeds *via* I and II.[14] Support for these intermediates was found from the following experiments.

An equimolecular mixture of II or phenyl isocyanate heated at 90° in the presence of NMM results in the formation of III and ethyl carbanilate. Using the same catalyst III is also isolated from a mixture of ethyl carbanilate and II. The formation of III from this mixture can be explained on the basis that the dimer is in reversible equilibrium with phenyl isocyanate monomer which can react with ethyl carbanilate to form I. The allophanate formed in this manner reacts with II to form III and ethyl carbanilate. Two experiments were run in order

to substantiate further the hypothesis that III arises from (a) dimer and (b) the isocyanate portion of allophanate.

A mixture of p-chlorophenyl isocyanate dimer and ethyl carbanilate was heated at 125° for 20 hours in the presence of a catalytic quantity of NMM. The sole product isolated was tri-p-chlorophenylisocyanurate in 50% yield. Under the same conditions and the same catalyst a mixture of p-chlorophenylisocyanate dimer and I produced a yield of 39.5% of a substance which analyzed correctly as a one-to-one mixture of tri-p-chlorophenylisocyanurate and 1-phenyl 3,5-di-p-chlorophenylisocyanurate. This mixture is probably due to the reaction of p-chlorophenyl isocyanate dimer and I to yield 1-phenyl 3,5-di-p-chlorophenylisocyanurate and ethyl carbanilate. In addition the reversible equilibrium formation of p-chlorophenyl isocyanate from p-chlorophenyl isocyanate dimer favors the formation of ethyl α-phenyl-γ,p-chlorophenylallophanate which can react with p-chlorophenyl isocyanate dimer to form tri-p-chlorophenylisocyanurate. In the absence of NMM the reactions leading to III do not proceed.

The infrared absorption spectra of unsubstituted allophanates prepared according to the procedure
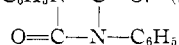
(10) H. L. Snape, *J. Chem. Soc.*, **49**, 254 (1886).
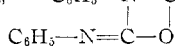
(11) M. Dennstedt, *Ber.*, **13**, 229 (1880).

(12) L. C. Raiford and H. B. Freyermuth, *J. Org. Chem.*, **8**, 230 (1934).

(13) E. Barthel, private communication.

(14) (a) H. Staudinger, ref. 8, postulates that the dimer exists in the symmetrical form, C_6H_5N—C=O. (b) N. G. Gaylord, J. A.

           O=C—N—C_6H_5

Snyder, *Chemistry and Industry*, 145 (1955), presented evidence to indicate that phenyl isocyanate dimer may exist in the unsymmetrical form, C_6H_5—N—C=O.   (c) In the crystalline state phenyl iso-
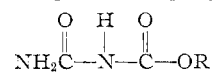
      C_6H_5—N=C—O

cyanate dimer has the symmetrical structure, C. J. Bowen, *J. Chem. Soc.*, 2931 (1955). Either structure can react with allophanate to give trimer.

$$\underset{NH_2C}{\overset{O}{||}}\!\!-\!\!\underset{N}{\overset{H}{|}}\!\!-\!\!\underset{C}{\overset{O}{||}}\!\!-\!\!OR$$

R = CH_3, $CH_3OCH_2CH_2$,–$CH_2CH_2OCH_2CH_2$–

of Blohm and Becker[15] have characteristic twin carbonyl absorption band at 5.70 and 5.86 μ. Similar bands at 5.74 and 5.90 μ appeared in the spectra of the substituted allophanates. The infrared absorption spectra of the trimers reported in this paper

(15) H. W. Blohm and E. I. Becker. THIS JOURNAL, **72**, 5342 (1950).

show an unusual characteristic. The results are tabulated in Table III.

TABLE III

INFRARED ABSORPTION SPECTRA

R	Absorption peak, μ	R	Absorption peak, μ
p-H	5.90	p-CH$_3$	5.68, 5.86, 5.94
o-CH$_3$	5.90	p-Cl	5.66, 5.85, 5.95
o-Cl	5.88	p-OCH$_3$	5.70, 5.83, 5.95
o-NO$_2$	5.87	p-NO$_2$	5.67, 5.83, 5.94
o-OCH$_3$	5.87		

Tri-(o-substituted-aryl)-isocyanurates have one carbonyl absorption band at 5.87–5.90 μ. This is in sharp contrast to the tri-(p-substituted-aryl)-isocyanurates whose spectra contain three main absorption peaks at 5.66–5.70, 5.83–5.86 and 5.94–5.95 μ. This single absorption band was also apparent with the trimers prepared from an aryl isocyanate and potassium acetate. Therefore it is not likely that allophanate, biuret and carbanilate could be contaminants. To allay any doubt that the trimers were not contaminated with dimer the compounds were refluxed for several hours with absolute ethyl alcohol. This procedure should result in the destruction of any dimer present by forming the carbanilate[6] but no carbanilate was isolated and the infrared absorption spectrum showed no change in the carbonyl absorption region.

Acknowledgment.—The author is indebted to Prof. J. D. Roberts and Dr. H. W. Bradley for many helpful suggestions during the course of this work.

Experimental[16,17]

Preparation of Intermediates.—The substituted ethyl carbanilates were prepared according to the procedure of Vittenet[18]: p-OCH$_3$, m.p. 64–65°; p-Cl, m.p. 66–67°; o-OCH$_3$, b.p. 107–108° (1 mm.); o-Cl, b.p. 119–120° (2 mm.); p-NO$_2$, m.p. 129–130°; o-CH$_3$, m.p. 44–45°; o-NO$_2$, m.p. 57–58°; methyl p-tolyl carbanilate was prepared in a similar fashion, m.p. 44–45°. *Anal.* Calcd. for C$_9$H$_{11}$O$_2$N: N, 8.4. Found: N, 8.3.

Preparation of Unsubstituted Allophanates.—The allophanates were prepared according to the procedure of Blohm and Becker[15] by bubbling cyanic acid into the proper alcohol. Methyl cellosolve yielded a white crystalline compound[18] which was recrystallized from methyl alcohol; it melted at 161–162° (163°).[19] The infrared absorption spectrum indicated a twin carbonyl peak at 5.70 and 5.86 μ. Diethylene glycol yielded a white crystalline diallophanate which was recrystallized with difficulty from water; it melted at 237–238°.

Anal. Calcd. for C$_8$H$_{14}$N$_4$O$_7$: C, 34.5; H, 5.06; N, 20.1. Found: C, 34.2; H, 5.10; N, 20.0.

The infrared absorption spectrum indicated a twin carbonyl peak at 5.70 and 5.85 μ. The derivative from methyl alcohol melted at 218.5° (208°,[20] 210°[21] and 212°[22]).

Preparation of I. Method (a).—A mixture of 35.7 g. (0.3 mole) of phenyl isocyanate and 16.5 g. (0.1 mole) of ethyl carbanilate was heated at 125–140° for 24 hours. The solution was cooled to room temperature and distilled *in*

(16) The author is indebted to the Analytical Section of Jackson Laboratory for the analytical data.

(17) All melting points are uncorrected.

(18) H. V. Henet, *Bull. soc. chim. France*, [9] **21**, 952 (1899).

(19) E. S. Lane, *J. Chem. Soc.*, 2764 (1951).

(20) L. Gattermann, *Ann.*, **244**, 29 (1888).

(21) A. E. A. Werner and J. Gray, *J. Sci. Proc. Roy. Dublin Soc.*, **24**, 77 (1946).

(22) A. Béhal, *Bull. soc. chim. France*, [4] **25**, 473 (1919).

vacuo. Thirty-one grams (89.5%) of unreacted phenyl isocyanate was obtained and converted to diphenylurea, m.p. 240–241°. The reaction was dissolved in ether and a small quantity of white crystals was obtained, m.p. 172–173°. A mixed melting point with an authentic sample of II, m.p. 175–176°, gave no depression. The solvent was removed and the residue crystallized from a mixture of petroleum ether (b.p. 30–60°) and carbon tetrachloride, 7.2 g. (22.9%), m.p. 92–94°. A mixed melting point with an authentic sample of I, m.p. 94–95°, gave no depression. The infrared spectrum indicated a twin carbonyl band at 5.85 and 5.90 μ.

Method (b).—A mixture of 35.7 g. (0.3 mole) of phenyl isocyanate and 2.3 g. (0.05 mole) of absolute ethyl alcohol was heated at 130° for 24 hours. The solution was cooled to room temperature and the excess phenyl isocyanate removed *in vacuo* (1 mm.), 26.2 g. (74%). The residue was cooled and 30 ml. of carbon tetrachloride was added; filtered off 0.3 g. of white platelets which melted at 174–175°. A mixed melting point with an authentic sample of II, m.p. 175–176°, gave no depression. To the filtrate was added 75 ml. of petroleum ether (b.p. 30–60°) and the solution was chilled in an ice-bath. A white crystalline product was obtained, weighing 3.2 g. (23%), m.p. 92–94°. A mixed melting point with an authentic sample of I, m.p. 94–95°, gave no depression.

Attempted Preparation of Ethyl α,p-Nitrophenyl-γ-phenylallophanate from Phenyl Isocyanate and Ethyl p-Nitrocarbanilate.—A mixture of 17.1 g. (0.144 mole) of phenyl isocyanate and 10.2 g. (0.0485 mole) of ethyl p-nitrocarbanilate was heated at 125° for 24 hours. The mixture was cooled to room temperature and 16.5 g. (96.5%) of phenyl isocyanate was removed *in vacuo*. The residue was dissolved in 50 ml. of ethyl alcohol and chilled for one hour. A light yellow compound was filtered, 9.8 g. (96.1%), m.p. 124–125°. A mixed melting point with a sample of ethyl p-nitrocarbanilate, m.p. 126–127°, gave no depression.

Preparation of Triarylisocyanurates.[23] Method (a).—The procedure of Hofmann[6] was followed in which an aryl isocyanate was heated in the presence of a small quantity of potassium acetate. Triphenylisocyanurate, m.p. 280–281° (274°[6,7]); molecular weight 357; found 368, benzene (ebullioscopic); tri-p-tolylisocyanurate, m.p. 264–265°, molecular weight 399; found 396, benzene (ebullioscopic); tri-p-methoxyphenylisocyanurate, m.p. 259–260°; tri-p-chlorophenylisocyanurate, m.p. 315–316°; tri-m-chlorophenylisocyanurate, m.p. 218° dec.

Anal. Calcd. for C$_{21}$H$_{12}$N$_3$O$_3$Cl$_3$: N, 9.2. Found: N, 9.7.

Tri-o-chlorophenylisocyanurate, m.p. 198–199°.

Method (b).—A mixture of 33.0 g. (0.278 mole) of phenyl isocyanate, 8.3 g. (0.05 mole) of ethyl carbanilate and 1.5 ml. of NMM was heated at 125°. At the end of 24 hours a temperature rise to 192° occurred and solid began to precipitate. The resulting mixture was allowed to cool and at approximately 180° it became completely solid. To the cooled solid was added 100 ml. of dry ether. The mixture was masticated thoroughly, washed with ether and filtered, 32.3 g. (98.8%), m.p. 280–281°. After the removal of the ether from the filtrate the residue was crystallized from petroleum ether, 7.8 g. (94%), m.p. 47–48°. A mixed melting point with an authentic sample of ethyl carbanilate, m.p. 48–49°, gave no depression.

Reaction of Phenyl Isocyanate and NMM.—A mixture of 66 g. (0.55 mole) of phenyl isocyanate and 3 ml. of NMM was heated for 40 hours at 125°. The mixture was cooled and divided into two equal portions. To one portion was added 1 g. of ethyl carbanilate and heated at 120°. After 16 hours a temperature rise occurred and a white crystalline solid precipitated. To the mixture was added dry ether and the solid was filtered and recrystallized from 95% ethyl alcohol, 31.4 g., 95% of III. m.p. 280–281°.

The second portion was heated at 125° for 16 hours; it yielded 0.9 g. (2.7%), m.p. 175–176° of II. The remaining phenyl isocyanate was converted to diphenylurea, 32 g. (97%), m.p. 240–241°.

Reaction between Phenyl Isocyanate and I in the Presence of NMM.—A mixture of 2.38 g. (0.02 mole) of phenyl isocyanate, 1.42 g. (0.005 mole) of I and 0.1 g. of NMM was heated on a steam-bath for 48 hours. Triphenylisocyanu-

(23) All the trimers reported in this paper were recrystallized from ethyl alcohol and verified by mixed melting point.

rate precipitated and was filtered and washed with five 10-ml. portions of dry ether, 1.8 g. (60.6%), m.p. 279–280°.

Reaction of Ethyl Carbanilate and II in the Presence of NMM.—A mixture of 11.9 g. (0.05 mole) of II, 8.3 g. (0.05 mole) of ethyl carbanilate and 1 ml. of NMM was heated at 125–130° for 48 hours. The mixture was cooled and 50 ml. of dry ether was added. The triphenylisocyanurate was filtered and washed with ether, 11.0 g. (99%), m.p. 278–279°. The filtrate was evaporated on a steam-bath and 100 ml. of petroleum ether (b.p. 30–60°) added, then chilled in an ice-bath for three hours. A white crystalline product was filtered off, 7.9 g. (95%), m.p. 47–48°. A mixed melting point with a sample of ethyl carbanilate, m.p. 48–49°, showed no depression.

Reaction of I and II in the Presence of NMM.—A mixture of 0.71 g. (0.00248 mole) of I and 0.590 g. (0.00248 mole) of II and one drop of NMM was heated on a steam-bath for 45 minutes until a hard crystalline solid was obtained. The solid was broken up with 20 ml. of ether and filtered, 0.798 g. (90%) of III, m.p. 280–281°. The filtrate was evaporated on a steam-bath and the residue was crystallized from petroleum ether (b.p. 30–60°). A white crystalline product 0.326 g. (80%), m.p. 47–48°, was obtained. A mixed melting point with a sample of ethyl carbanilate, m.p. 48–49°, showed no depression.

Reaction between p-Chlorophenyl Isocyanate Dimer and I in the Presence of NMM.—A mixture of 1.42 g. (0.005 mole) of I, 1.53 g. (0.005 mole) of p-chlorophenyl isocyanate dimer and one drop of NMM was heated at 100° for three hours. The mixture was cooled in an ice-bath and 5 ml. of ether was then added. The white insoluble material was filtered off and recrystallized from ethyl alcohol, 0.8 g. (39.5%), m.p. 239–240°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Cl_3$ plus $C_{21}H_{13}N_3O_3Cl_2$: N, 9.9; Cl, 19.9. Found: N, 9.7; Cl, 19.4.

The infrared spectrum indicated the mixture had absorption peaks at 5.66, 5.85 and 5.95 μ.

Reaction between p-Chlorophenyl Isocyanate Dimer and Ethyl Carbanilate in the Presence of NMM.—A mixture of 1.53 g. (0.005 mole) of p-chlorophenyl isocyanate dimer, 0.83 g. (0.0029 mole) of ethyl carbanilate and one drop of NMM was heated for 24 hours at 100°. The mixture was then cooled and 10 ml. of ether added. A white crystalline product was filtered and recrystallized from ethyl alcohol, 1.15 g. (75%), m.p. 313–314°.

Anal. Calcd. for $C_{21}H_{12}N_3O_3Cl_3$: N, 9.2. Found: N, 9.0.

Reaction of Phenyl Isocyanate and Absolute Ethanol.—A mixture of 35.7 g. (0.3 mole) of phenyl isocyanate, 2.3 ml. (0.05 mole) of absolute ethyl alcohol and 1 ml. of NMM was heated for 24 hours at 125°. The mixture was cooled and 20 ml. of ether was added. Triphenylisocyanurate was filtered, 35.0 g. (98%), m.p. 280–281°. After the removal of the solvent from the filtrate, 60 ml. of petroleum ether (b.p. 30–60°) was added. A white crystalline product was obtained, 7.1 g. (86%), m.p. 48–49°. A mixed melting point with an authentic sample of ethyl carbanilate, m.p. 48–49°, gave no depression.

Infrared Absorption Spectra.—Infrared absorption spectra were determined with a Perkin–Elmer infrared spectrophotometer #21. No solvent was used. The spectra were determined as Nujol mulls in a demountable cell using sodium chloride windows with 0.025 mm. spacers (normal thickness).

WILMINGTON, DELAWARE

The Question of Orientation in the Introduction of the Triphenylmethyl Radical into Solvent Substrates of Toluene, Chlorobenzene and Methyl Benzoate. The Tritylation of Aromatic Rings Containing Deactivating Groups

BY ROBERT A. BENKESER AND REX B. GOSNELL

Several errors in the literature have been detected, particularly in connection with the structural assignments of *m*- and *p*-tritylbenzoic acids. The inference that the trityl radical (in the presence of benzoyl peroxide) enters *exclusively* into the *para* position of various solvent substrates like toluene, chlorobenzene and methylbenzoate to form *para*-substituted tetraphenylmethanes has been disproved. It has also been found that triphenylcarbinol reacts with *o*-chloroaniline, *o*-nitroaniline and anthranilic acid in the presence of hydrochloric acid. In each case the trityl group entered the ring *para* to the amino group forming a 3,4-disubstituted tetraphenylmethane. These represent some of the first successful tritylation reactions of rings containing deactivating groups.

The acid-catalyzed reaction of triphenylcarbinol with aromatic rings containing activating groups (tritylation reactions) has been known for some time.[1-4] Presumably the reaction proceeds *via* an attack of the triphenylmethylcarbonium ion on the *para*-position of the activated aromatic ring. *Ortho*-substitution is generally prevented by the large steric requirements of the trityl group.

$$(C_6H_5)_3COH \xrightarrow{H^+} (C_6H_5)_3C^+ \xrightarrow{C_6H_5—R} p\text{-}(C_6H_5)_3C—\!\!\langle\;\rangle\!\!—R$$
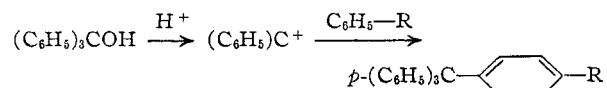
R = activating group

No cases have been reported in which such a reaction has been successful with aromatic rings containing deactivating groups such as nitro or carboxyl. This is not surprising since the triphenyl-methyl carbonium ion is stabilized considerably by resonance and consequently reacts only sluggishly. Accordingly it can be expected to attack only highly activated rings and these only at positions of high electron density.[5]

Recently we had occasion to investigate several preparative routes leading to *m*- and *p*-tritylbenzoic acids. In the course of this study it was discovered that *o*-chloroaniline, *o*-nitroaniline and anthranilic acid condense with triphenylcarbinol, despite the deactivating group each of them contains. While the yields are not high in the two latter cases, the reaction provides a very convenient method for obtaining certain 3,4-disubstituted tetraphenylmethanes. In every case the trityl group enters *para* to the amino group as would be expected.

The structure of compound I was established by deaminating it to *m*-tritylchlorobenzene. An au-

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