(b) By dehydration of 3-trifluoromethyl-2-buten-1-ol. 2-Trifluoromethyl-2-buten-1-ol (45 g., 0.32 mol.) was added slowly with external cooling to phosphoric oxide (42.6 g., 0.3 mol.) in a 500-ml. flask equipped as above in part (a) above and stirred without heating until a uniform paste was formed. Heat was then applied and 23 g. of crude product obtained. Fractionation gave 22 g. (60.3%) of 2-trifluoromethylbutadiene-1,3, b.p. 36°, n_{D}^{22} 1.3434. Infrared spectra of this sample were identical with that of the sample prepared by the dehydration of 2-trifluoromethylbutadiol-2,3.

α-Trifluoromethylacrylonitrile. The equipment used for pyrolysis of trifluoroacetone cyanohydrin acetate consisted of the following: A flowmeter for measuring the volume of nitrogen and a dropping funnel for the acetate were connected to one end of a 1 × 12 in. Pyrex tube packed with borosilicate beads. The Pyrex tube was heated by a combustion furnace to 500 ± 5° and the internal temperature automatically controlled by a thermocouple and pyrometer. Pyrolyzed material was led directly from the furnace into an ice-water cooled receiver equipped with a reflux condenser. A tube connected the top of the reflux condenser to two cold traps in Dry Ice and acetone.

A typical reaction was carried out as follows: Acetate (45 g.) was added in 57 min. Nitrogen was added at the rate of 10 l. per hour. The crude product (37.5 g.) was fractionated to give 14.0 g. (46.6%) of 2-trifluoromethylacrylonitrile, b.p. 73–85°.

Trifluoromethylacrylonitrile has the following physical properties: b.p. 78–79°, $n_{\mathrm{D}}^{26.4}$ 1.3261, $d_{\mathrm{D}}^{26.4}$ 1.1753.

Anal. Calcd. for $C_4H_2F_3N$: MR_D 20.79. Found: MR_D 19.96. Lit.,[4] b.p. 75.9–76.2°, n_{D}^{20} 1.3239.

Reaction of methylmagnesium bromide with α-trifluoromethylacrylonitrile. Two mol. of methylmagnesium bromide was prepared in a 2-l., three-neck flask from 2.00 mol. (48.6 g.) of magnesium and enough methyl bromide to react completely with it in 1 l. of dry ether. To this cold solution was added trifluoromethylacrylonitrile (212 g., 1.75 mol.) dissolved in 200 ml. of dry ether. After refluxing for 4 hr., during which time a wax-like precipitate formed, 10% sulfuric acid was added and the precipitate dissolved. The ether solution was separated and the water layer extracted with additional ether. After drying and removal of the ether, fractionation gave 15 g. of material with the following properties: b.p. 127–127.5°, n_4^{27} 1.4108, d_4^{27} 0.9350.

Anal. Found: C, 49.7; H, 5.99; N, 9.13.

GAINESVILLE, FLA.

[CONTRIBUTION NO. 158 FROM THE CENTRAL RESEARCH LABORATORIES OF
MINNESOTA MINING AND MANUFACTURING CO.[1]]

The Chemistry of Xylylenes. IV. The Stabilization of Benzyl Radicals in Solution

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Received May 11, 1959

Solutions of benzyl radicals, in concentrations as high as 10^{-4} molar, were prepared by fast flow pyrolysis of toluene at low pressure and subsequent condensation of the pyrolyzate into a solvent kept at −78°. Solvated radicals were still present 1.5 hr. after termination of pyrolysis. Surprisingly, an equal amount of *p*-xylylene was also accumulated during the reaction. Apparently this was formed by dehydrogenation of *p*-xylene produced *via* methylation of toluene. The unusual stability of solvated benzyl radicals at −78° may be a manifestation of complex formation with toluene thereby decreasing their rate of coupling.

It has been reported by one of us[3] that solutions of extremely reactive compounds such as *p*-xylylene can be prepared by instantaneous condensation of its low pressure stream into a suitable solvent kept at low temperature. This technique was also applied successfully to the preparation of solutions of benzyl radicals, albeit in low concentration. Thus, 500 g. toluene, metered at the rate of 0.03 mol./min., was pyrolyzed at 1000°, 4 mm. pressure, and 0.004 sec. residence time, and the pyrolyzate was condensed at −78° into 4.5 l. toluene. Iodometric titration of an aliquot sample indicated that about 1.5×10^{-3} equivalents of active species had accumulated in the final solution. The concentration of titratable species decreased steadily at −78° from 3×10^{-4} molar to 3×10^{-5} molar over a period of 90 min. and thereafter decreased very slowly to 1×10^{-5} molar over a period of 28 hr.

Apparently this was a mixture of two active compounds. The more stable species, despite the fact that it decolorized test solutions of diphenylpicrylhydrazyl, was not a free radical since negative results were obtained when an aliquot of this solution, that had been aged for 20 hr., was analyzed in an electron spin spectrometer.[4]

Gas chromatography and infrared analysis indicated that the pyrolysis feed stock (b.p. 110–111°) used in these experiments was 99.8% toluene, 0.1% benzene, and 0.1% aliphatic hydrocarbon. The presence of xylenes was not detected in even a trace amount. The composition of the condensate obtained as a result of its pyrolysis at 970° and 0.02 sec. residence time was 97.2% toluene, 1.1% dibenzyl, 0.7% benzene, 0.4% ethylbenzene, 0.4%

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(1) A portion of this work was carried out in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Co. with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Co. in March 1957.

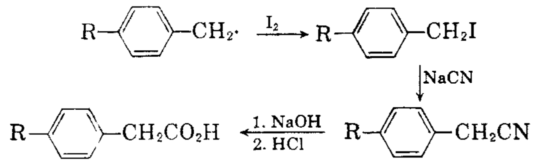
(2) Present address: The M. W. Kellogg Co., Jersey City, N. J.

(3) L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, **79**, 4952 (1957).

(4) The authors are indebted to Professor John Wertz of the University of Minnesota for use of the electron spin spectrometer.

diphenylmethanes, 0.2% anthracene, <0.1% aliphatic hydrocarbon, a trace amount of xylenes, which was mostly *o*-xylene, and a trace amount of stilbene. Hydrogen and methane were also produced during the pyrolysis as noncondensable gases. None of the above compounds react with diphenylpicrylhydrazyl and with iodine at −78°.

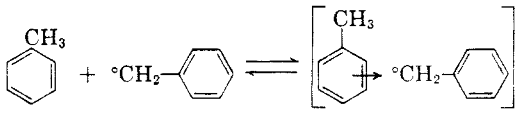
In order to identify the two active species, a second solution, prepared as described above and containing about 10^{-3} mol. titratable product, was quenched at −78° with excess iodine to convert the reactive molecules to the corresponding iodides. Since these are unstable compounds and are present as only minor components in a complex mixture of pyrolysis products, no attempt was made to isolate them as such. Instead the iodides were converted to the corresponding cyanides and these, in turn, were saponified to afford the corresponding carboxylic acids. In this experiment 0.5 g. phenylacetic acid and 0.3 g. *p*-phenylenediacetic acid were isolated from the reaction mixture whereas no acidic products were isolated in a control experiment starting with 0.2*N* iodine in toluene solution. These results demonstrate that the active species present in the original solution were benzyl radical and *p*-xylylene in amounts at least as great as those of the mono and dibasic acids isolated.



p-Xylylene is a very reactive diamagnetic compound[5] and is known to exist for many hours in solution at −78°.[3] This undoubtedly was the more stable transient species. It must have formed pyrolytically in gas phase *via* methylation and subsequent thermal dehydrogenation,[6] since methane, benzene and xylenes were identified as products of toluene pyrolysis. No significant increase in yield of acids was realized when the pyrolyzate was condensed at −78° directly into hexane saturated with iodine. This indicates that virtually all the benzyl radicals couple in gas phase to afford dibenzyl before they reach the quench solution.

Solutions of benzyl radicals in extremely viscous solvents at room temperature have been prepared photochemically by Porter and Windsor.[7] The decay time was measured in milliseconds, whereas it was too rapid to follow in a nonviscous solvent such as hexane. This difference in reactivity was attributed to the radical's relative mobility in the two solvents.

The present observation, however, cannot be explained on this basis, since the solvents used were nonviscous liquids. This is clearly a case of decreased reactivity of the solvated radical at low temperature which can best be interpreted in terms of π-complex formation as postulated by Russell[8] and Walling[9] or in terms of σ-complex formation as postulated by Wheland.[10]



Dissociation of such a complex should increase markedly with temperature, and hence coupling of the "liberated" radicals is extremely rapid at room temperature whereas it is relatively slow at −78°. Assuming that the decay time of a 10^{-4} molar solution of benzyl radicals at room temperature is only a matter of milliseconds as reported by Porter and Windsor,[7] then the activation energy for the over-all reaction is about 14 kcal. Actually this thermal dependence may be a direct measure of the stability of the complex, since it is known that the activation energy for coupling of radicals in gas phase is almost zero.

EXPERIMENTAL

Pyrolysis of toluene. In all these experiments chemically pure toluene (b.p. 110–111°) purchased from Merck and Co., Inc., was used as the pyrolysis feed stock. Gas chromatography and infrared analysis indicated that its composition was 99.8% toluene, 0.1% benzene, and 0.1% aliphatic hydrocarbon. No evidence for the presence of even trace amounts of xylenes (or higher aromatic hydrocarbons) was detected despite deliberate attempts to identify these components. Five hundred g. of this feed stock (5.4 mol.) was subjected to fast flow pyrolysis at 970° C., 5 mm. pressure, and 0.02 sec. residence time as described previously.[3] The pyrolyzate was condensed at −78°. The volatile components (480 g., b.p. <140°) were separated by distillation at atmospheric pressure. Its composition was determined by gas chromatography and infrared analysis to be 98.9% toluene, 0.7% benzene, 0.4% ethylbenzene, <0.1% aliphatic hydrocarbon, and a trace amount of xylenes, most of which was *o*-xylene. The residue (2 3 g., b.p. >140°C.) was separated by distillation at 1 mm. Hg. pressure. The first fraction (1.9 g., b.p. 85–100°) was recrystallized from methanol at −78° to afford 1.5 g. crude dibenzyl which, when recrystallized from fresh methanol, was obtained as white crystals (m.p. 49–50°). The methanol mother liquors were evaporated to dryness leaving 0.4 g. oil as residue. This was identified by infrared analysis as a mixture of diphenylmethane and 2-methyldiphenylmethane with a small amount of stilbene also present. The second fraction (0.25 g.; b.p. >100°) was identified by infrared analysis as impure anthracene. This was purified by sublimation and subsequent recrystallization from methanol to afford a sample of pure anthracene in the form of white platelets (m.p. 210–212°).

Thus, 5.4 mol. toluene were metered to the system and 5.1 mol. were recovered. The rest was converted to 0.04 mol. benzene, 0.02 mol. ethylbenzene, 0.007 mol. dibenzyl, 0.002 mol. diphenylmethane, 0.001 mol. anthracene, and trace amounts of xylenes and stilbene. The materials balance

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(5) L. A. Errede and J. M. Hoyt, *J. Am. Chem. Soc.*, in press.

(6) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

(7) G. Porter and M. W. Windsor, *Nature*, **180** 187 (1957).

(8) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

(9) C. Walling and M. W. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

(10) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

accounts for 96% of the phenyl groups metered into the furnace. No attempt was made to isolate quantitatively the noncondensable gases since we and others[6] have shown previously that these are mostly hydrogen and methane.

Preparation and disappearance of active species in solution. Toluene (500 g.) was vaporized at atmospheric pressure and the gas was metered at the rate of 0.03 mol./min. to the evacuated pyrolysis system described previously.[3] The gas was pyrolyzed at 1000°, 4 mm. pressure, and 0.004 sec. residence time, and the pyrolyzate was condensed at $-78°$ in 4.5 l. toluene. The disappearance of accumulated titratable species was followed iodometrically at $-78°$. Two 100-cc. aliquot samples were removed periodically by means of a prechilled pipette. The first was used as a blank. This was warmed to room temperature and then added to 20 cc. of $0.01N$ iodine. The second was added at $-78°$ to the same volume of $0.01N$ iodine. The excess iodine in each flask was back titrated with $0.0192N$ aqueous $Na_2S_2O_3$, and the difference noted was a measure of titratable species. The results are summarized below:

Time (Hr.)		0	1	1.5	2	10	20	30
Concentration mol./l.	10^4	2.6	1.3	0.3	0.2	0.1	0.1	0.08

Identification of benzyl radical and p-xylylene. A second 4-l. solution of pyrolyzate in hexane was prepared as described above via fast flow pyrolysis of 500 g. toluene. The solution contained about 10^{-3} mol. of titratable species when it was quenched at $-78°$ with excess iodine. The resulting solution was warmed to room temperature and the excess iodine was reduced with aqueous sodium thiosulfate. The organic solvent was removed by evaporation and 11 g. dark oil was obtained as residue. This was made to react at 50° with 10 g. NaCN in 200 cc. water methanol solution (1 to 1) over a period of 4 hr. The mixture was separated by extraction with ether. The ether extract was evaporated to dryness leaving a dark oil. This was leached with hot aqueous NaOH for 4 hr. The aqueous solution was acidified and extracted with ether. Infrared analysis indicated that the dark alkali insoluble oil was essentially a mixture of the usual products of fast flow pyrolysis of toluene, namely dibenzyl, and diphenylmethanes. The ether extract was evaporated to dryness leaving 1.1 g. of acidic material as residue. This was separated by vacuum sublimation. The more volatile acid fraction (0.5 g.) was recrystallized from hexane in the form of white needles (m.p. 74.5–76.0°). Its mixed melting point and its infrared spectrum identified the compound as phenylacetic acid. The less volatile fraction (0.3 g.) was recrystallized from hot water in the form of long white needles (m.p. 243–245°). This was identified as *p*-phenylenediacetic acid since its mixed melting point and its infrared spectrum were identical with that of the authentic sample. In another experiment the pyrolyzed toluene stream was condensed at $-78°$ directly into 4 l. hexane saturated with iodine and thereafter the procedure was followed as described above. Again only 1.5 g. acidic material was obtained. Its infrared spectrum indicated that this was a mixture of phenylacetic acid and *p*-phenylenediacetic acid. As a control experiment, 4 l. of $0.2N$ I_2 in toluene solution was treated as described above and no acidic products were isolated. The above results indicate therefore that benzyl radical and *p*-xylylene were present in the original solution in at least the amounts of corresponding acids isolated.

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[CONTRIBUTION OF THE FULMER CHEMICAL LABORATORY, WASHINGTON STATE UNIVERSITY]

Nonbasic Character of Some Aminotrifluoromethyldiphenyl Sulfones Synthesis of 3-Amino-5-trifluoromethyldiphenyl Sulfone[1]

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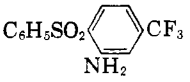
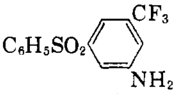
Received May 15, 1959

2-Amino-4-trifluoromethyldiphenyl sulfone (I) and the corresponding bis sulfone IV exhibit extreme nonbasic character by their insolubility in hot 30% hydrochloric acid and lack of reactivity with typical amino group reagents. Such behavior is explained by the strong inductive effect of the sulfone group on an *ortho*-amino group and by enhancement through hydrogen bonding of the resonance interaction involving amino and sulfone groups. Derivative formation in this unreactive series of amino sulfones was accomplished by reaction with acetic anhydride in the presence of a catalytic amount of sulfuric acid to give acetamido compounds. Several studies involving synthesis and structure confirmation of 3-amino-5-trifluoromethyldiphenyl sulfone (II) are described.

It has been found that 2-amino-4-trifluoromethyldiphenyl sulfone (I) exhibits some surprisingly nonbasic properties. It is virtually insoluble in 30% hydrochloric acid and fails to react with acetyl chloride, benzenesulfonyl chloride, or phenyl isothiocyanate to give amino derivatives.[3] Because of these observations, it became of interest to study a group of aminotrifluoromethyldiphenyl sulfones, and especially the isomers of I, 3-amino-5-trifluoromethyldiphenyl sulfone (II) and 4-amino-2-trifluoromethyldiphenyl sulfone (III).


I


II


III

The basicity of these amines was evaluated qualitatively by relative solubility in hot or cold hydrochloric acid of varying concentrations, and the results are summarized in Table I. It is to be

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[1] Presented in part at the 1956 Northwest Regional Meeting of the American Chemical Society, Seattle, Wash., June 12.

[2] In part abstracted from a thesis submitted by C. Richard Bresson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Washington State University, June 1958.

[3] In part, these experiments were carried out by Richard C. Thamm, Senior in Chemistry, 1952–53.