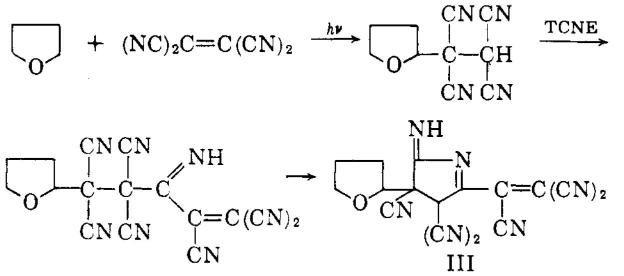
spectrum of I in deuterated acetone has single peaks at 2.11 and 3.95 τ and multiple peaks centered at 5.41, 6.11, and 7.93 τ in a ratio 4.2:0.99:1.0:2.0:4.2 which supports the proposed structure. Furthermore, the 7- and 8-positions of TCNQ have been shown previously to be the sites of attack by free radicals.[2] The identity of the photo-reduced product II was established by comparison with a known sample.[2]

A solution of tetracyanoethylene (TCNE) in tetrahydrofuran also underwent a facile reaction when irradiated with a GE sunlamp. The colorless, crystalline product III had the composition of two moles of TCNE to one mole of tetrahydrofuran. An n.m.r. spectrum of the product in deuterated acetone showed a broad peak centered at 0.85 τ, and multiple peaks at 3.95, 5.95, and 7.9 τ in a ratio of 0.87:0.98:2.0:4.2. On standing, the peak at 0.85 τ gradually disappeared, and the broad peak at 7.9 τ increased in intensity by one proton due to exchange with the solvent, giving rise to the C–H peak of acetone.

Since the n.m.r. spectrum of III shows the presence of a mono-α-substituted tetrahydrofuran group, apparently the primary 1:1 photoaddition product underwent subsequent fast ionic addition to a neutral molecule of TCNE. The following over-all process is considered as one possibility.



III

The proposed conjugated cyclic imidine structure for III is in accord with its extensive ultraviolet absorption, its infrared spectrum, and its n.m.r. spectrum which showed the presence of a readily exchangeable proton. The primary photoaddition step across the ethylenic double bond rather than across a nitrile group is postulated in analogy to other free-radical additions to TCNE[3] and in analogy to the addition of tetrahydrofuran to TCNQ as previously discussed. The subsequent ionic addition to the nitrile group of another TCNE molecule explains the extensive ultraviolet absorption of III. Because of the present lack of suitable ultraviolet model compounds, any structure assignment concerning the bonding of the cyanocarbon moiety can only be tentative. In the n.m.r. spectrum, the shift of the tertiary α-hydrogen atom by 2.4 p.p.m. from that of tetrahydrofuran itself demonstrates an extremely strong field effect by the substituent group.

Experimental

Preparation of I by Irradiation.—A solution of 3.5 g. of TCNQ in 500 ml. of tetrahydrofuran was irradiated with a GE sunlamp for 8 hr. The solvent was then removed under reduced pressure. The residual brown oil solidified on rubbing with a benzene–petroleum ether mixture. On extraction with hot toluene and subsequent cooling, there was obtained 2.5 g. (55%) of round, off-white crystals, m.p. 136–139°. Recrystallization from a large volume of a benzene–cyclohexane mixture gave I as white rods, m.p. 138–140°.

Anal. Calcd. for $C_{16}H_{12}N_4O$: C, 69.6; H, 4.4; N, 20.3. Found: C, 69.8; H, 4.4; N, 20.3.

The insoluble residue, 0.3 g. (8.5%), m.p. 242–245°, proved to be *p*-phenylenedimalononitrile (II)[2] by comparison of its infrared spectrum with that of an authentic sample. Admixture with an authentic sample did not lower its melting point.

A 10^{-3} molar solution of TCNQ in tetrahydrofuran upon a 20-min. exposure to sunlight no longer showed any absorption due to TCNQ (395 mμ, ϵ 63,600). No reaction took place in the dark.

Preparation of I by Initiation with Di-*t*-butyl Peroxide.—A solution of 1.5 g. (0.0075 mole) of TCNQ and 0.07 g. (0.0005 mole) of di-*t*-butyl peroxide in 250 ml. of tetrahydrofuran was heated in a shaker tube for 4 hr. at 150°. The solvent was then removed under reduced pressure. The residual oil dissolved to a large extent in hot benzene. On filtration and cooling, there was obtained 0.65 g. (33%) of I, m.p. 138–140°, mixture melting point with sample of I prepared by irradiation, 138–140°.

The undissolved residue, 0.15 g. (10%), proved to be *p*-phenylenedimalononitrile.

Preparation of III.—A solution of 50 g. of TCNE in 350 ml. of tetrahydrofuran was irradiated for 4 days with a GE sunlamp. The solution was clear and had a dark red-brown color. The solvent was then removed under reduced pressure, leaving 54 g. of dark residue. Extraction of the residue with 800 ml. of hot benzene afforded 24 g. (37%) of purple solid on cooling. A portion of this solid was recrystallized from a mixture of 400 ml. of benzene and 5 ml. of acetonitrile to give shiny, white crystals of III, m.p. 172° dec.

Anal. Calcd. for $C_{16}H_8N_8O$: C, 58.5; H, 2.4; N, 34.2; mol. wt., 328. Found: C, 58.7; H, 2.6; N, 34.1; mol. wt., 326 (b.p. in acetone).

The infrared spectrum of III shows bands at 3.10 (NH), 4.45 (conjugated CN), 6.08 (attributed to $N{-}\overset{|}{C}{=}N{-}$), and at 6.45 μ (conjugated C=C); $\lambda_{\max}^{CH_3CN}$ 218 (22,800), 227 (21,600), 257 (5680), and 271 mμ (5960). TCNE, for comparison, absorbs at 256 (8100), 263 (9360), and 272 mμ (10,000).

The product III shows only very limited stability. On standing in the solid state, it slowly turns red. This process is accelerated in polar solvents.

---

[2] D. S. Acker and W. R. Hertler, *J. Am. Chem. Soc.*, **84**, 3370 (1962).

[3] W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *ibid.* **80**, 2783 (1958).

Trimethyl Trichlorohemimellitate from an Unusual Fragmentation Reaction

J. DIEKMANN

Contribution No. 846 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received May 23, 1963

A convenient path to bicycloheptadienes lies in the Diels–Alder reaction of cyclopentadienes with suitable acetylenes. Thermolysis of the resulting adduct leads to benzene derivatives in favorable circumstances. Thus, tetraphenylcyclopentadienone and diphenylacetylene on heating react to form hexaphenylbenzene and carbon monoxide.[1] Similarly, the reaction of phenylacetylene with 5,5-dimethoxytetrachlorocyclopentadiene affords 2,3,4,5-tetrachlorobiphenyl in low yield,[2] while the reaction of 5,5-dimethoxytetrachlorocyclopentadiene with 2-butynediol diacetate has been reported to give tetrachloro-1,2-diacetoxybenzene.[3]

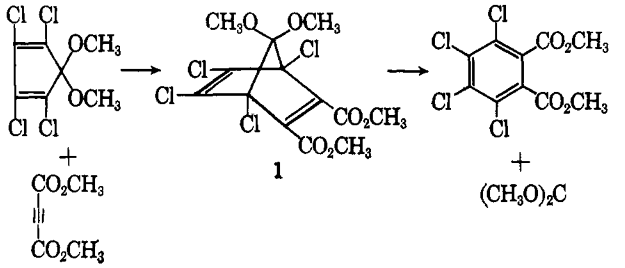
---

[1] W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

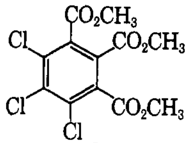
[2] E. T. McBee, *et al.*, *J. Am. Chem. Soc.*, ,**77** 385 (1955).

[3] H. Feichtinger and H. Linden, German Patent 1,105,862 (1961).

By an analogous scheme, we hoped to prepare the bicycloheptadiene **1**, a potential precursor to dimethoxycarbene, which can be considered the dimethyl ketal of carbon monoxide.



When equimolar amounts of 1,1-dimethoxytetrachlorocyclopentadiene and dimethyl acetylenedicarboxylate were heated to 150°, a product was obtained which was neither the expected bicycloheptadiene **1** nor dimethyl tetrachlorophthalate. Instead, the product had the composition of trimethyl trichlorohemimellitate **2**, another possible fragmentation product from **1**.



2

The structure assignment of **2** is supported by its n.m.r. spectrum which shows two unsplit peaks separated by 4 c.p.s. at 60 Mc. in a ratio of 2:1. Confirmation of the molecular weight came from the mass spectrum which showed the presence of the parent peak at m/e = 354; the observed isotope pattern confirms the presence of only three chlorine atoms.[4]

A similar fragmentation appears to be involved in the debromination of 1,2,3,4-tetrachloro-5,6-dibromo-7,7-dimethoxybicyclo[2.2.1]hept-2-ene with zinc in refluxing acetic acid to give methyl 2,3,4-trichlorobenzoate.[5]

Experimental

A mixture of 9.9 g. (0.037 mole) of 5,5-dimethoxytetrachlorocyclopentadiene and 5.3 g. (0.037 mole) of dimethyl acetylenedicarboxylate was heated to 150° at which temperature an exothermic reaction set in. Heating was continued for 10 min. On cooling, the brown mixture solidified. Recrystallization of the crude product from ethanol gave 8.2 g. (62%) of trimethyl trichlorohemimellitate as colorless crystals, m.p. 93–94°; $\lambda_{\max}^{CH_3CN}$ 222 (41,600), 292 (754), and 302 mμ (ε 704).

Anal. Calcd. for $C_{12}H_9Cl_3O_6$ (355.56): C, 40.54; H, 2.55; Cl, 29.93. Found: C, 40.54; H, 2.40; Cl, 30.37.

When the Diels–Alder components were heated in refluxing xylene or toluene, **2** was formed in 75% yield.

---

[4] Independently of us, Professor Lemal of the University of Wisconsin has attempted preparation of dimethoxycarbene by the same route. His findings agree with ours. Furthermore, he has also identified methyl chloride as the other fragmentation product. We wish to thank Professor Lemal for communication of his results prior to publication.

[5] K. Mackenzie, *J. Chem. Soc.*, 457 (1962).

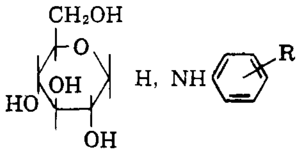
Ionization Constants of Some *N*-Aryl-D-glucosylammonium Ions

Robert Smith, Sandra Holton, and Olaf Runquist

Department of Chemistry, Hamline University,
St. Paul 1, Minnesota

Received June 18, 1962

During the course of work in our laboratory on the hydrolysis rates of glucosylamines, it became necessary to investigate the ionization constants of certain glucosylammonium ions. Six glucosylamines (I) were selected for this study: (a) *N*-phenyl-, (b) *N*-*m*-tolyl- (c) *N*-*p*-tolyl-, (d) *N*-*p*-anisyl-, (e) *N*-*p*-chlorophenyl-, and (f) *N*-*p*-fluorophenyl-D-glucosylamine. Each of these compounds was prepared from the corresponding aromatic amine and glucose. The pK_a values for the glucosylamines were determined spectrophotometrically by a modification of the method described by Flexser, Hammett and Dingwall.[1]



I

Ia, R = H
b, R = m-CH_3
c, R = p-CH_3
d, R = p-OCH_3
e, R = p-Cl
f, R = p-F

The aryl-D-glucosylamines are stable in basic solution but undergo rapid hydrolysis in acid media.[2a,b] This hydrolysis makes the direct determination of pK_a very difficult and limits the experimental techniques which can be used. This paper describes an attempt to estimate the pK_a of some glucosylamines by a back-extrapolation method through which some of the difficulties associated with the instability of the aryl-D-glucosylamines in acid solution have been overcome.

The ultraviolet spectra of all glucosylamines studied were similar to those of the corresponding aromatic amine, and the absorptivity of the solutions decreased with increasing acidity. Therefore, it should be possible to determine the molar absorptivity of the glucosylammonium ion and the glucosylamine by measuring the absorbance of solutions at sufficiently high and low acidity, respectively. The molar absorptivity of the glucosylamines was readily measured in solutions that were 10^{-4} M in sodium hydroxide. The rapid hydrolysis of glucosylamines[2a,b] in acidic solutions makes the direct determination of the molar absorptivity of the protonated glucosylamines impossible. Because of the similarities of the glucosylamines to the anilines, we assumed that the molar absorptivity of the glucosylammonium ion would be small and that little error would be introduced by neglecting the absorptivity of this species. Other methods of determining pK_a when

---

[1] L. A. Flexser, L. P. Hammett, and A. Dingwall, *J. Am. Chem. Soc.* **57**, 2103 (1935).

[2] (a) S. Holton and O. Runquist, *J. Org. Chem.*, **26**, 5193 (1961); (b) W. W. Pigman, E. A. Cleveland, D. H. Couch, and J. H. Cleveland, *J. Am. Chem. Soc.*, **73**, 1976 (1951).