81, 108 (1959).

(29) L. E. Friedrich and R. A. Fiato, *J. Org. Chem.*, **39,** 2267 (1974).

(30) R. Breslow and H. Won Chang, *J. Am. Chem. Soc.*, **83,** 2367 (1961).

(31) H. Normandt, *Adv. Org. Chem.*, **2,** 1 (1960).

(32) C. F. H. Allen and W. E. Barker, *J. Am. Chem. Soc.*, **83,** 2367 (1961).

(33) (a) 3,3-Dimethylacrylophenone was prepared by the reaction of excess phenyllithium with 3,3-dimethylacrylic acid. The spectral properties (NMR) were identical to those previously reported (see ref 32). (b) For an alternative preparation of the enone, see G. Darzens, *C. R. Hebd. Seances Acad. Sci.*, **189,** 766 (1929), and (c) J. M. Watson, J. L. Irvine, and R. M. Roberts, *J. Am. Chem. Soc.*, **95,** 3349 (1973).

(34) T. Mukaiyama, K. Soai, and K. Narasaka, *Chem. Lett.*, 1223 (1974).

(35) H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34,** 2324 (1969).

(36) J. Normandt, J. DuBois, and G. Schutz, *Bull. Soc. Chim. Fr.*, 3578 (1966).

(37) H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, **79,** 1920 (1957).

(38) W. Adam, J. Baeza, and J. Liu, *J. Am. Chem. Soc.*, **94,** 2000 (1972).

(39) Confer with H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **96,** 5143 (1974).

(40) D. A. Evans, G. L. Carroll, and J. K. Trusdale, *J. Org. Chem.* **39,** 914 (1974).

(41) J. A. Marshall, N. G. Anderson, and P. C. Johnson, *J. Org. Chem.*, **35,** 186 (1970).

(42) L. Meites and T. Meites, *Anal. Chem.*, **20,** 984 (1948).

(43) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. London, Ser. B*, **140,** 470 (1953).

(44) The retention times varied somewhat; however, the calibration factors remained constant.

Photodecomposition of Diethyl Mercurybis(diazoacetate) in Several Heterocyclic Systems[1a]

Timothy B. Patrick* and Tai-Teh Wu[1b]

Department of Chemistry, Southern Illinois University, Edwardsville, Illinois 62026

Received October 11, 1977

The products from the photolysis of diethyl mercurybis(diazoacetate) (1) in the solvent–reactant systems of tetrahydrofuran, tetrahydrothiophene, and pyrrolidine were studied for the determination of the relative importance of the various competing photodecomposition modes. Regioselective insertion reactions into carbon–hydrogen bonds α to the heteroatom were observed, whereas carbon–heteroatom insertion reactions were not observed. Analysis of the organic products, mercury, and nitrogen indicated that carboethoxycarbyne ($:\dot{C}CO_2Et$(A)) could account for 10–30% of the yields of α carbon–hydrogen insertion products. Mercury-containing products from the photodecomposition of 1 in pyrrolidine solution gave evidence for major participation of a mercury carbene (B) intermediate. The evidence also showed that other reaction paths were of little importance.

Monovalent carbon atoms, carbynes, represent an intriguing and little studied class of chemical intermediates. Diethyl mercurybis(diazoacetate) (1),[2] Buchner's compound, has been studied by Strausz et al. and was observed to furnish carboethoxymethyne (A) in low but usable yield under proper photolytic conditions.[3]

$$\underset{\textbf{1}}{Hg(N_2CCO_2C_2H_5)_2} \qquad \underset{\text{A}}{:\dot{C}CO_2C_2H_5}$$

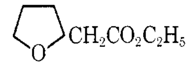
We previously reported that photolysis of 1 in chlorocarbon solvents gave products that could arise from association between A and the chlorine atoms; however, the reactions were very complex.[4]

We initiated the study reported here with the objective of finding less complicated reactions that would permit better definition of the photodecomposition paths followed by 1 and allow a better description of the chemistry of the intermediates involved. The heterocyclic solvent–reaction systems of tetrahydrofuran (THF), tetrahydrothiophene (THT), and pyrrolidine were chosen for study because their geometries are well defined and the heteroatom electronic effects are predictable.[5] Thus, meaningful rationalization of the photodecomposition routes and intermediates involved could be obtained from the study of their reaction products.

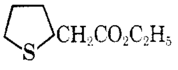
Results

Photolysis of 1 in THF and THT. Photolysis of 1 in THF gave N_2, Hg, and ethyl α-(tetrahydrofuranyl)acetate (2). Compound 2 was formed in good yield but was not isolated in a good state of purity. Direct hydrolysis of the reaction mixture containing 2 furnished α-(2-tetrahydrofuranyl)acetic acid in 41% yield. Comparison of the acid with a sample prepared unambiguously (see the Experimental Section) served to establish the correct α insertion structure. Products from insertion into either the β carbon–hydrogen bond or the carbon–oxygen bond were not observed.[6]

Photodecomposition of 1 in THT solution gave ethyl α-(2-tetrahydrothienyl)acetate (3) in 54% yield. This product from α-carbon–hydrogen insertion was identified through its spectral characteristics which were similar to those of 2 and through conversion of the crude reaction product to the corresponding acid in 30% yield. The structure of the acid was confirmed by spectral analysis. The THT system, similar to the THF system, did not yield products resulting from insertion into either the β-carbon–hydrogen bonds or the carbon–sulfur bond.[6]



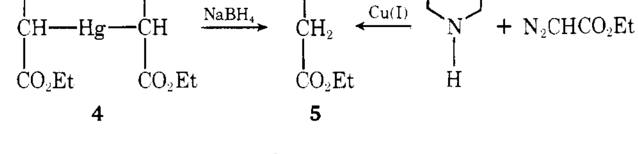
2 (>41%)



3 (54%)

Olefinic products were observed in small amounts by NMR spectroscopy, but their structures were not determined. Product analysis was performed after nitrogen evolution had ceased even though mercury formation was not complete at that time (Table I).

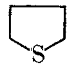
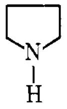
Photolysis of 1 in Pyrrolidine. Three products were isolated from the photolysis of 1 in pyrrolidine. The major product, **4,** was isolated in 48% yield. The structure of 4 was determined from spectral properties and from sodium borohydride reduction[7] to ethyl α-(N-pyrrolidino)acetate (5). A



4 5

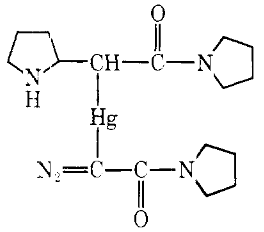
0022-3263/78/1943-1506$01.00/0

Table I. Mercury and Nitrogen Yields

			
(1) Maximum N_2 Yield, %	90	70	100
(2) Time, min	80	100	60
(3) Hg yield at max N_2 yield, %	20	27	33
(4) Maximum Hg yield, %	70	70	90
(5) Time, min	180	240	170
(6) $2Hg/N_2$ at time = 0	0.19	0.31	0.29
(7) Primary Hg yield, %	9–18	10–21	15–29

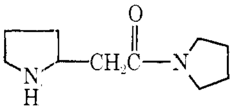
sample of **5**, prepared unambiguously from the copper(I)-catalyzed decomposition of ethyl diazoacetate in pyrrolidine,[8] was identical with the product obtained from reduction.

Another mercury-containing product (**6**) was isolated in 19% yield. Compound **6** was sensitive to the light and deposited mercury on standing. Structure **6** should be considered tentative, but spectroscopic evidence shows that **6** is a diazomercury compound.



6 (19%)

Compound **7**, formed from insertion into the α-carbon–hydrogen bond, was isolated in 20% yield. Spectral data were used to determine the structure of **7**. Olefinic products were not observed in the pyrrolidine photolysis reaction.



7 (20%)

Control experiments in THF and pyrrolidine solutions containing ethyl diazoacetate showed that the products observed from **1** were not formed in a route in which **1** was first converted to ethyl diazoacetate followed by photolysis since the control runs were significantly different in the number and types of products obtained. Additionally, dark reaction control experiments with **1** gave no evidence for any significant reactions occurring in the absence of light. Attempts to determine quantum yields were unsuccessful because of the heterogenicity induced from the mercury precipitation.

Mercury and Nitrogen Yields. Mercury and nitrogen yields were accurately determined for all solvent–reactant systems. A plot of the $2Hg/N_2$ ratio (eq 1, Discussion) vs. photolysis time was made and the ratio at $t = 0$ is reported in Table I. The plot could extrapolate to a value of unity if only primary processes occur; a smaller value indicates the fraction of primary process operative.[3] Secondary photolysis processes of mercury-containing intermediates are responsible for the value being less than unity. The extrapolated $2Hg/N_2$ values show a primary Hg yield of 9–21% in THF and THT and a yield of 15–29% in pyrrolidine. The mercury yield equals the carbyne yield in the processes shown by eq 1 and 2 below.

Discussion

The major photodecomposition paths considered for **1** are:[3]

$$\underset{1}{Hg(N_2CCO_2C_2H_5)_2} \xrightarrow{h\nu} Hg + 2N_2 + \underset{A}{:\dot{C}CO_2C_2H_5} \qquad (1)$$

$$1 \rightarrow Hg + N_2 + \underset{A}{:\dot{C}CO_2C_2H_5} + N_2\dot{C}CO_2C_2H_5 \qquad (2)$$

$$1 \rightarrow N_2 + \underset{B}{C_2H_5O_2C\ddot{C}\text{-}HgC(N_2)CO_2C_2H_5} \qquad (3)$$

$$1 \rightarrow Hg + \underset{C}{2N_2\dot{C}CO_2C_2H_5} \qquad (4)$$

$$1 \rightarrow Hg + N_2 + \underset{D}{2C_2H_5OCOCN} \qquad (5)$$

Only processes 1 and 2 simultaneously yield N_2, Hg, and A. Analysis of the $2Hg/N_2$ ratio for process 1 as a function of time and extrapolation to time equals zero gave the results shown in Table I. The mercury yield obtained from the $2Hg/N_2$ extrapolation for process 1 equals the carbyne (A) yield; the carbyne yield is one-half the mercury yield if process 2 is used. Thus the carbyne (A) yield in THF and THT solutions is 9–21% and 15–29% in pyrrolidine solution. Prolonged photolysis, after N_2 evolution had ceased, resulted in higher mercury yields indicating that processes other than 1 and 2 are also operative.

The photodecomposition paths followed in both THF and THT solutions appear similar since reaction times and product yields are nearly the same. However, in pyrrolidine solution the photodecomposition paths may be influenced by the solvent since reaction times are shorter, product yields are higher, and mercury-containing materials are observed.

All reactions show an extremely high degree of selectivity for insertion into the α-carbon–hydrogen bond. This could indicate that the intermediate involved in the insertion is associated to a high extent with the heteroatom, or that the heteroatom polarizes the α-carbon–hydrogen bond sufficiently to account for the selectivity.[5,6] If the former case holds, it is unusual that insertion into the carbon–heteroatom is not observed since this is observed in many carbenic reactions.[6]

The mercury-containing compounds, **4** and **6**, observed in the pyrrolidine system give good evidence that process 3 is operative. In fact, process 3 is the major process in this reaction as 67% of the total material balance is found in **4** and **6**. Thus, B is a major intermediate in the reaction.

Process 4 is considered unlikely because reaction energetics favor $C{=}N_2$ bond breakage over C–Hg bond cleavage,[3] and no evidence for the presence of ethyl diazoacetate, formed from C, was obtained. Process 5 is probably inoperative since complete nitrogen evolution was observed and the presence of D could not be confirmed even though reaction conditions would have permitted detection of D.

An estimate of the amount of carbyne participation in the pyrrolidine system can be made as follows. During the nitrogen evolution period, mercury is obtained in 33% yield; after nitrogen evolution stops, mercury is accounted for to the extent of 62% yield in isolated mercury-containing products. These mercury-containing products give a 0.5% yield of mercury per minute on prolonged photolysis. Therefore, the yield of products possible during the nitrogen evolution period from mercury-containing products is 9.9%. The yield of nonmercury products above 9.9% may be attributed to carbyne participation. In the case of α-insertion product **7**, isolated in 20% yield, 11% can come from carbyne and 9.9% can occur from mercury-containing products.

Application of this approach to the THF system gives a 10% yield contribution from carbyne A; in the THT system, a 30% contribution from the carbyne is possible. However, the estimates are weakened for these systems because mercury-containing products were not isolated.

The estimation of carbyne participation depends largely on the use of mercury and nitrogen yields based on hypothetical photodecomposition paths and also relies on the exclusion or determination of other possible reaction intermediates. Beneficial information can be obtained from this approach, but future work will require a more direct carbyne analysis method.

Conclusions

Photodecomposition of 1 in the systems studied suggests that the solvent may influence the reaction course to some extent. However, the major photodecomposition intermediate is the diazomercury carbene (B) while carboethoxycarbyne (A) may account for approximately 10–20% of the reaction.[9] These intermediates show a high degree of selectivity for insertion into the α-carbon–hydrogen bonds.[10] Furthermore, carbon–heteroatom insertion is completely absent, a sharp contrast with the chemistry of carboalkoxycarbenes.[11]

Experimental Section[12]

General Photolysis Procedure. Freshly prepared 1 (0.400 g, 0.937 mmol) was dissolved in 4.0 mL of the solvent system and placed in an 8 in. × 0.5 in. Vycor tube equipped with a rubber septum and gas release needle. The degassed solution was irradiated with a Havovia 450-W medium pressure, mercury-arc vapor lamp equipped with a Vycor filter and water-cooled (20 °C) jacket. The photolysis was carried to 80–90% completion as monitored from the amount of nitrogen evolved. The mercury precipitate was filtered and the filtrate was worked up as specified.

Tetrahydrofuran Solution. Mercury (0.047 g, 25%) was filtered, and the filtrate containing 2 was hydrolyzed to the acid with aqueous sodium hydroxide solution. The acidified solution was extracted thoroughly with ether, dried, and concentrated to give 0.104 g (41%) of α-(α-tetrahydrofurfuryl)acetic acid as a yellow semisolid which was identified by comparison with an authentic sample prepared as described below.

α-(2-Tetrahydrofuryl)acetic Acid. In a 500-mL three-necked flask equipped with a mechanical stirrer, dropping funnel, and thermometer were placed 50 g (0.50 mol) of reagent grade 2-tetrahydrofurfuryl alcohol (Aldrich) and 46 g (0.59 mol) of pyridine.

Freshly distilled thionyl chloride, 63 g (0.53 mol), was added dropwise to the rapidly stirred mixture which was maintained at a temperature below 60 °C with an ice bath. After complete addition, the mixture was stirred for an additional 4 h. The mixture was thoroughly extracted with ether. The ether extracts were dried and concentrated to give crude 2-tetrahydrofurfuryl chloride.

In a 500-mL, three-necked flask equipped with a stirrer, dropping funnel, and condenser were placed 5.8 g (0.12 mol) of sodium cyanide, 5 mL of water, and 15 mL of *N*,*N*-dimethylformamide. The crude 2-tetrahydrofurfuryl chloride (14.1 g, 0.12 mol) was added to the cyanide solution. The mixture was stirred at reflux for 16 h. Distillation of the mixture up to 160 °C removed most of the solvents. The remaining solution of 2-tetrahydrofurfuryl cyanide was hydrolyzed with sodium hydroxide solution. The basic solution was extracted with ether and acidified. The acidic mixture was extracted with ether, dried, and concentrated to give α-(2-tetrahydrofuryl)acetic acid as a yellow semisolid, identical with the acid obtained from the hydrolyzed photolysis solution: IR (neat) 3632–2341 (COOH), 1732 (C=O), 1300–1130 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.30 (s, 4 H, CH_2), 2.50 (d, 2 H, *J* = 7 Hz, CH_2), 3.38–3.98 (t, 2 H, *J* = 7 Hz, CH_2), 3.96–4.55 (m, 1 H, *J* = 7 Hz, CH); MS *m/e* 130 (33, P), 113 (19, P − OH), 85 (10, P − COOH). Anal. Calcd for $C_6H_{10}O_3$: C, 55.38; H, 7.69. Found: C, 55.12; H, 7.70.

Ethyl α-(2-tetrahydrofuryl)acetate (2) was prepared by heating a mixture of the acid, absolute ethanol, and hydrogen chloride at reflux for 2 h. The oily product had identical spectral properties with that of a crude sample obtained from chromatography of the photolysis mixture: IR (neat) 2922 (CH), 1732 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.00–1.50 (m, 7 H, ring protons and CH_3), 2.50 (d, 2 H, *J* = 7 Hz, CH_2), 3.34–3.90 (t, 2 H, *J* = 7 Hz, CH_2), 3.90–4.54 (m, 3 H, CH_2, CH); MS *m/e* 158 (5, P), 113 (25, P − OC_2H_5), 85 (3, P − $CO_2C_2H_5$), 71 (44, P − CH_2, $CO_2C_2H_5$).

Tetrahydrothiophene Solution. After nitrogen evolution, the mercury (0.056 g, 30%) was removed, and the filtrate was hydrolyzed to the acid by th procedure used for THF. The α-(2-tetrahydrothienyl)acetic acid weighed 0.105 g (35%). Sublimation at 100–120 °C (0.5 mm) furnished white needles: mp 32–33 °C; IR (KBr) 3582–2432 (COOH), 1710 (C=O), 1150–1300 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.25 (s, 4 H, CH_2), 2.51 (d, 2 H, CH_2), 3.32–4.0 (m, 2 H, CH_2), 4.0–4.6 (m, 1 H, CH); MS *m/e* 146 (17, P), 101 (8, P − COOH), 86 (51, P − CH_2, COOH). Anal. Calcd for $C_6H_{10}SO_2$: C, 49.32; H, 6.85; S, 21.92. Found: C, 49.28; H, 6.79; S, 21.88.

Ethyl α-(2-Tetrahydrothienyl)acetate (3). Chromatography of the combined filtrates from four reactions on a 10 in. by 0.75 in. column of alumina ($CHCl_3$/CH_2Cl_2, 1:1) gave 3 in the first 25-mL eluent as a yellow oil, 0.191 g (53.9%). Resolve-Al*[13] (Aldrich) was added to 3 in $CDCl_3$. The obscured methylene doublet at δ 1.57 was clearly shifted downfield to δ 3.27: NMR ($CDCl_3$) δ 1.10–1.36 (m, 7 H, CH_2CH_3, and ring protons), 3.27 (d, 2 H, *J* = 7 Hz, CH_2), 4.0–4.6 (m, 5 H, CH_2CH_3, and ring protons); IR (neat) 2952 cm^{-1} (CH), 1732 (C=O), 680 (CS); MS *m/e* 174 (6, P), 146 (14, P − C_2H_5), 101 (10, P − $CO_2C_2H_5$), 86 (54, P − CH_2, $CO_2C_2H_5$).

Pyrrolidine Solution. The photoysis mixture was filtered (Hg, 0.065 g, 35%) and the concentrated filtrate was chromatographed on a 4.5 in. by 0.75 in. alumina column with $CHCl_3$, CH_2Cl_2, and CH_3OH as successive solvents. The first three 25-mL fractions from chloroform elution contained three components which were separated on an alumina column (8 in. by 0.25 in.; $CHCl_3$) and collected in 10-mL fractions.

Component I was identified as ethyl α-mercurybis[α-(N-pyrrolidino)acetate] (4) as a tan semisolid: 0.23 g (48%); IR (neat) 3200–2780 (CH), 1732 (C=O), 1300–1150 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.15–1.50 (t, 6 H, *J* = 7 Hz, CH_3), 1.60–2.00 (m, 8 H, CH_2), 2.50–3.00 (m, 8 H, CH_2), 3.45 (s, 2 H, CH), 3.90–4.50 (g, 4 H, *J* = 7 Hz, OCH_2); MS *m/e* 157 (4, P − Hg, $C_8H_{14}NO_2$, $CO_2C_2H_5$), 70 (100, P − Hg, $C_8H_{14}NO_2$, CH_2, $CO_2C_2H_5$). Anal. Calcd for $C_{16}H_{28}N_2O_4Hg$: C, 27.84; H, 4.18; N, 6.50. Found: C, 27.80; H, 4.28; N, 6.72.

Component II was identified as *N*,*N*-tetramethylene-α-pyrrolidinoacetamide (7), a yellow semisolid: 0.068 g (20%); IR (neat) 3600–3100 (NH), 1632 (C=O), 1250 (CN), 909 cm^{-1} (NH); NMR ($CDCl_3$) δ 1.25 (s, 4 H, CH_2), 1.60–2.30 (m, 7 H, ring protons) 2.40 (d, 2 H, *J* = 8 Hz, 2-CH_2), 3.35–3.80 (m, 4 H, ring protons), 7.20–7.70 (m, 1 H, NH); MS *m/e* 182 (37, P) 112 (19, P − C_4H_8N), 84 (47, P − C_4H_8N, CO), 70 (100,P − C_4H_8N, CO, C_4H_8N). Anal. Calcd for $C_{10}H_{18}N_2O$: C, 65.93; H, 9.89; N, 15.38. Found: C, 66.06, H, 9.96; N, 15.15.

Component III was tentatively assigned structure 6 on the basis of spectral analysis: unstable yellow oil, 0.092 g (19%); IR (neat) 3600–2500 (NH), 1684 (C=O), 2184 (C=N_2), 1250 (CN), 909 cm^{-1} (NH); NMR ($CDCl_3$) δ 1.20–1.34 (m, 4 H, CH_2), 1.70–2.40 (m, 10 H, ring protons), 2.80 (d, 1 H, *J* = 7 Hz, HgCH), 3.20–3.95 (m, 9 H, ring protons).

Ethyl α-(N-Pyrrolidino)acetate (5). Ethyl diazoacetate (7.98 g, 0.07 mol) was added dropwise to a stirred mixture at 5–10 °C of pyrrolidine (14.91 g 0.21 mol) and cuprous cyanide (1.57 g, 0.017 mol). After complete addition, the mixture was stirred for 5 h at 5–10 °C. The brown mixture was filtered and extracted thoroughly with chloroform. The concentrated chloroform mixture was distilled at 110–150 °C (0.1 mm) to give 5 as a yellow oil in 77% yield. Anal. Calcd for $C_8H_{15}NO_2$: C, 61.15: H, 9.55; N, 8.92. Found: C, 60.96; H, 9.32; N, 8.99.

Reaction of 4 (0.06 g) with excess sodium borohydride in chloroform produced mercury and 5 which had identical spectral properties with those of an authentic sample: IR (neat) 2930–2882 (CH), 1730 (C=O), 1300–1140 cm^{-1} (CO); NMR ($CDCl_3$) δ 1.05–1.35 (t, 3 H, *J* = 7 Hz, CH_3), 1.60–2.00 (m, 4 H ring protons, 2.40–2.80 (m, 4 H, ring protons), 3.30 (s, 2 H, CH_2), 3.95–4.30 (q, 2 H, *J* = 7 Hz, CH_2); MS *m/e* 157 (26, P), 128 (5, P − C_2H_5), 84 (12, P − $CO_2C_2H_5$), 70 (7, P − $CO_2C_2H_5$, CH_2).

Mercury and Nitrogen Yields. Solutions containing 0.40 g (0.937 mmol) of 1 in the appropriate solvent were placed in Vycor tubes and subjected to photolysis. At various time intervals (5–15 min), the nitrogen evolution was determined from water displacement. The sample was removed from photolysis and the mercury precipitate weight was recorded. At least eight data points were used for the t = 0 extrapolations reported in Table I. An error of 10–15% was calculated for these experiments. Fluctuations in lamp intensity and the presence of the mercury precipitate are thought to be responsible for this error.

Registry No.—**1,** 20363-85-3; **2,** 2434-02-8; **3,** 65102-19-4; **4,** 65102-20-7; **5,** 22041-19-6; **6,** 65102-21-8; **7,** 1078-64-4; α-(α-tetrahydrofurfuryl)acetic acid, 2434-00-6; 2-tetrahydrofurfuryl alcohol, 97-99-4; 2-tetrahydrofurfuryl chloride, 3003-84-7; 2-tetrahydrofurfurylcyanide, 33414-62-9; α-(2-tetrahydrothienyl)acetic acid, 65102-22-9; ethyldiazoacetate, 623-73-4; pyrrolidine, 123-75-1.

References and Notes

(1) (a) This research was supported by the Office of Graduate Research, Southern Illinois University at Edwardsville. (b) Taken in part from the M.S. Thesis of Tai-Teh Wu, Southern Illinois University at Edwardsville, 1976.

(2) E. Buchner, *Chem. Ber.*, **28**, 215 (1895).

(3) O. P. Strausz, G. J. A. Kennepohl, F. X. Garneau, T. DoMinh, B. Kim, S. Valenty, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5723 (1974), and references cited therein.

(4) T. B. Patrick and G. H. Kovitch, *J. Org. Chem.*, **40**, 1527 (1975).

(5) R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds", 2nd ed, Interscience, New York, N.Y., 1967, pp 62–140.

(6) Carbene reactions, on the contrary, show less discrimination of reaction sites as many carbon–hydrogen and carbon–heteroatom insertion reactions have been reported. W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971, Chapter 11.

(7) See S. J. Valenty and P. S. Skell, *J. Org. Chem.*, **38**, 3937 (1973), for the synthetic utility of this type of reaction.

(8) T. Saegusa, Y. Ito, S. Kobayaski, K. Hirota, and T. Shimizu, *Tetrahedron Lett.*, 6131 (1966).

(9) Drs. P. S. Skell and S. J. Valenty have independently concluded that the diazomercury carbene (B) is the major intermediate formed in the photolysis of **1**. Private communication from Professor Skell.

(10) Mercury-containing carbenes do not undergo carbon–hydrogen insertion into ordinary hydrocarbons: P. S. Skell and S. J. Valenty, *J. Am. Chem. Soc.*, **95** 5042 (1973).

(11) A. P. Marchand and N. M. Brockway, *Chem. Rev.*, **74**, 431 (1974).

(12) All temperature readings are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and were within ±0.3% of the theoretical values. A Varian T-60 spectrometer was used for ^{1}H NMR analyses with tetramethylsilane as the internal reference. A Varian MAT-111 spectrometer was used for mass spectral analyses at 80 eV. A Perkin-Elmer Model 337 spectrometer calibrated with polystyrene was used for infrared analyses.

(13) See, R. E. Sievers, Ed., "Nuclear Magnetic Resonance Shift Reagents", Academic Press, New York, N.Y., 1973, for a review.

Carbon-13 Chemical Shift Response to Substituent Effects in Arylmethyl and Arylhydroxy Carbenium Ions. Evidence for Substituent Interaction in Disubstituted Ions Depending upon the Carbenium-like Character at the Trigonal Carbon

B. Ancian, F. Membrey, and J. P. Doucet*

Laboratory of Physical Organic Chemistry, The University of Paris VII (Associated with CNRS), 75005 Paris, France

Received September 16, 1977

The interrelations between the ^{13}C NMR shielding effects of para substituents and electronic structure have been investigated in diphenylmethyl and diphenylhydroxy carbenium ions 1 and **2**. The prime dependence of the ^{13}C shieldings upon π charge delocalization effects is established. It is shown that a general description of the chemical shifts, valid on all sites, requires using both π-electron density and π-bond order terms, as illustrated by the correlation obtained at ca. 120 ppm. While for the substituted ring carbons the SCS remain nearly the same as for neutral monosubstituted benzenes, the substituent shifts at C_α are increased by 2.7 in ions 1 as compared to **2**, thus showing that electronic effects at this position are strongly dependent on the withdrawing power of the carbenium center (as confirmed by the unusually small effects of acceptor substituents). Nonadditivity of the C_α SCS in some 4,4′-disubstituted ions demonstrates the existence of important interactions between substituent electron effects. These interactions can be accounted for with the concept of a concerted π-inductive-mesomeric effect: the electron transfer from a substituent to the carbenium center depends upon the demand of this center and therefore upon all the other groups present. The susceptibility of the substrate to these interactions is estimated by a I_{XY} term (expressed with a $\sigma_X{}^+\sigma_Y{}^+$ product) and related to the carbenium character. Long range effects at the unsubstituted ring result from a π-inductive effect without π-electron transfer from the substituent. The C_α bridge acts only as a relay whose efficiency is directly related to the magnitude of its positive charge.

A great deal of attention has been focused over the last years on carbenium ions as they are key intermediates in many organic reactions. In this field, NMR spectroscopy, especially ^{13}C NMR, appears to be one of the most suitable techniques for a charge-delocalization investigation in cations,[1] although Brown[2a] and Kramer[2b] have pointed out that some problems may occur in relating ^{13}C shifts and carbenium ion stabilities. Much of the literature is devoted to the study of substituent effects on the chemical shifts of aryl carbenium ions for which the unusual stabilities have been ascribed to delocalization of positive charge throughout the π-electron system of the aromatic rings. Substituent chemical shifts[3] (SCS) have been chosen as a probe of the ability of groups to disperse the positive charge and have been compared to substituent parameters (generally Brown or Taft constants) deduced from solvolytic reactions in which the transition state is postulated to approximate the character of these ions.[4–6]

The relationships between shieldings and semiempirical MO have been extensively investigated by Olah et al.[7] The fact that, for carbons remote from the carbenium center, the π charge densities are as good as total charge densities in correlating the observed shifts is a definite proof that the dominant influences on screenings are π-system resonance and polarization interactions; moreover, the slope of their regression line[7a] is very close to the usual proportionality constant of 160 ppm/electron density obtained in a large variety of aromatic systems.[1,8] Farnum's point of view[1a] is slightly different, since he uses the total charge density with the questionable assumption of no charge dispersion to the hydrogens. Ray, Kurland, and Colter[5] have also shown that carbon chemical shifts in trityl cations are well correlated with CNDO/2 charges, whereas the crude HMO electron densities poorly reflect the trends. However, a great dispersion of quaternary ipso and α carbons can usually be observed, while an impossibility to describe all the shifts by a general expression using only electron density, whatever the carbons, is also evident.[2] This situation has prompted us to reexamine the possible contribution of other terms—like π-bond orders—to the carbon shielding in aryl carbenium ions. The important question of the additivity of substituent effects in ions is also open to challenge. If saturation of their electronic influences is now a fairly well-documented experimental phenomenon,[6,9–14] its interrelation with the extent of a positive charge at the relevant nuclei is not yet elucidated. Con-

0022-3263/78/1943-1509$01.00/0