was further oxidized with dichromate and acid to 1,7-dimethyl-4-carboxycarbostyril. Decarboxylation of this product led to a substance which melted at 105–107°. This agrees with the reported melting point for 1,7-dimethylcarbostyril.[6]

EXPERIMENTAL[7]

The 1,4-dimethyl and 1,3,4-trimethylcarbostyrils have been previously reported.[4,6] 1,4,6- and 1,4,7-Trimethylcarbostyrils are new compounds and were prepared by the action of diketene on *p*-N-methyltoluidine and *m*-N-methyltoluidine. The description of the preparation of one of these compounds follows.

1,4,6-Trimethylcarbostyril. A mixture of 33.9 g. (0.28 mole) of *p*-N-methyltoluidine and 50 ml. of benzene was heated to reflux. Diketene (34.5 g., 0.41 mole) was added dropwise over a period of 3 hr. The benzene was removed under reduced pressure and the residue poured into 100 ml. of concentrated sulfuric acid in 5-ml. portions so as to keep the temperature below 70°. The sulfuric acid mixture was then heated on the steam bath for 15 min. This mixture was then poured into 1 l. of ice water and neutralized with solid sodium hydroxide. After standing overnight the solid was collected and crystallized from ethanol. A recrystallization of the product from ethanol-water gave a white product melting at 106–107°. The yield was 90%.

Anal. Calcd. for $C_{12}H_{13}NO$: N, 7.48. Found N, 7.17.

1,4,7-Trimethylcarbostyril. This compound was prepared in an exactly analogous manner starting with *m*-N-methyltoluidine. The yield was 93.5% and the compound melted at 103–104°. No other compound was isolated. This compound and 1,4,6-trimethylcarbostyril are both prone to retain large quantities of alcohol from the solvent, and constant melting points can be obtained only after lengthy drying in vacuum over anhydrous calcium chloride.

Anal. Calcd. for $C_{12}H_{13}NO$: N, 7.48. Found: N, 7.15.

1,6-Dimethyl-4-formylcarbostyril. This compound was obtained (38% yield) as lemon-yellow needles, m.p. 181–183°, by a method previously described.[8]

Anal. Calcd. for $C_{12}H_{11}NO_2$: N, 6.96. Found: N, 7.21.

1,7-Dimethyl-4-formylcarbostyril. This compound was obtained (69% yield) as orange-yellow needles, m.p. 185–187°, by a method described earlier.[8]

Anal. Calcd. for $C_{12}H_{11}NO_2$: N, 6.96. Found: N, 6.91.

1,6-Dimethyl-4-carboxycarbostyril. A mixture of 8 g. (0.039 mole) of 1,6-dimethyl-4-formylcarbostyril and 3.51 g. of sodium dichromate (0.0134 mole) was suspended in 100 ml. water and mixed with a mechanical stirrer. Thirteen and one-tenth g. of concentrated sulfuric acid was added dropwise. After addition was complete the mixture was heated on the steam bath for 30 min. After cooling in ice the solid was collected and dissolved in 22 ml. of a 5% sodium hydroxide solution and filtered. Upon acidification of the filtrate with hydrochloric acid, 19.8 g. (61%) of the product was obtained. Recrystallization of a sample from ethanol and water gave pale yellow crystals which charred at 270° and decomposed at 290–295°.

Anal. Calcd. for $C_{12}H_{11}NO_3$: N, 6.45; Neut. equiv., 217. Found: N, 6.70; Neut. equiv., 220.

1,7-Dimethyl-4-carboxycarbostyril. This compound was prepared in a manner analogous to that described above. The substance decomposed at 238–240°.

Anal. Calcd. for $C_{12}H_{11}NO_3$: N, 6.45. Found: N, 6.78.

1,7-Dimethylcarbostyril. A 2.4-g. sample (0.011 mole) of 1,7-dimethyl-4-carboxycarbostyril was ground with 1.5 g. of soft glass and placed in a small distilling flask. The flask was left open to the air and heated in a Wood's metal bath at a temperature of 300–350° for 24 hr. At the end of this time the liquid was distilled under a pressure of 2 mm. The red-orange distillate solidified on cooling and was recrystallized from 15 ml. petroleum ether (35–60°) containing a few drops of benzene to bring the product into solution. A m.p. was 87–97°. A vacuum sublimation of this substance gave pale yellow needles, m.p. 105–107°. The reported m.p. is 107–108°.[6]

Acknowledgment. The financial aid received from the Du Pont Co. of Willmington, Del., by one of the authors (D. J. C.) in the form of a summer research grant is acknowledged with appreciation.

GREENCASTLE, IND.

---

[6] A. Kent, D. McNeal, and R. M. Cowper, *J. Chem. Soc.*, 1858 (1939).

[7] Melting points are uncorrected.

[8] Cook and Stamper, *J. Am. Chem. Soc.*, **69**, 1467 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

Fulvenes. III. Heat of Combustion and Resonance Energy[1]

JESSE H. DAY AND CHARLES OESTREICH[2]

Received July 30, 1956

The heats of combustion and the calculated resonance energies are reported for dimethylfulvene and diphenylfulvene. The reported values are consistent with the known properties of the fulvenes.

Although the fulvenes have been known for more than half a century[3] and many theoretical calculations made of the resonance energy of fulvene,[4] no experimental data for the estimation of resonance energies have appeared. This paper reports the heats

---

[1] Taken in part from the M.S. thesis of Charles Oestreich, June 1956.

[2] Present address, Department of Chemistry, Virginia Military Institute.

[3] J. Thiele, *Ber.*, **33**, 666 (1900).

[4] For a list of references see J. H. Day, *Chem. Revs.*, **53**, 167 (1953). Also see B. Pullman and A. Pullman, *Les Theories Electroniques de la Chimie Organique*, Masson et Cie, Paris, 1952.

of combustion and calculated resonance energies for dimethylfulvene and diphenylfulvene.

The data for the heats of combustion are summarized in Table I. These values and the resonance energy values in Table II should prove of value in the explanation and prediction of the chemical properties of the fulvenes. The methods of molecular orbitals and of valence bonds have in the past agreed less well for fulvene than for most other hydrocarbons, and the present data may prove useful in this connection.

TABLE I

REPRESENTATIVE DATA FOR THE HEATS OF COMBUSTION OF DIMETHYLFULVENE

Run	Weight Sample, G.	Calorimeter Temp. rise °C.	Heat Evolved in Cal.	HNO_3 Corr.	Fuse Wire Corr.	Capsule Wt.	Capsule Corr.	Net Heat in Kcal./Mole[a]
1	0.7312	6.112	15004	31.0	30.0	0.1425	1142	1113.2
2	.6521	5.522	13556	28.4	22.5	.1462	1223	1115.5
3	.6623	5.542	13605	27.2	30.0	.1292	1093	1114.3
4	.6847	5.767	14157	31.3	32.5	.1439	1153	1114.7
5	.5028	4.322	10601	23.6	35.0	.1303	1049	1114.7
		Representative Data for the Heats of Combustion of Diphenylfulvene						
1	0.3007	2.160	5301.6	9.4	25.0			2241.3
2	.3708	2.659	6527.6	11.9	28.5			2238.6
3	.3961	2.851	6999.0	11.6	38.0			2244.8
4	.3017	2.175	5339.4	10.6	34.0			2241.4

[a] The last column is the net heat evolved at constant volume. When the Washburn correction is made, and the heat of combustion corrected to constant pressure at 25° with reactants and products in their standard states, the average values become, for dimethylfulvene 1116.1 kcal./mole, for diphenylfulvene 2243.7 kcal./mole. The values at 25° and 1 atmosphere pressure for the reactants and products in the gaseous state are estimated to be for dimethylfulvene 1125.0 kcal./mole, for diphenylfulvene 2268.7 kcal./mole. (The water equivalent of the calorimeter at 25° was 2454.9 ± 0.9; the gelatine capsules had a heat of combustion of 8015 B.t.u./lb.)

TABLE II

RESONANCE ENERGIES OF TWO FULVENES

	Heat of Combustion[a]		Resonance Energy, Kcal./Mole
	Calcd.	Exper.	
Dimethylfulvene	1136.9	1125.0	11.9
Diphenylfulvene	2354.1	2268.7	85.4

[a] The calculated heats of combustion were made using the table of Klages' values as reported in Wheland.[5]

Much of the work that has been done with fulvenes has not required a high degree of purity. In this work considerable care was taken to insure maximum purity; the details are described in the experimental section.

The resonance energies were calculated by the usual subtraction of the measured heat of combustion (corrected to be that for gaseous reactants to gaseous products at 25°) from the theoretical value calculated using the tables compiled by Klages. Use of Franklin's tables[5] gives slightly higher values of the resonance energy. The data on the heat of vaporization of dimethylfulvene were calculated from a plot of the logarithm of the vapor pressure against the reciprocal of the temperature, and found to be 10.56 kcal./mole. The needed heat of sublimation of diphenylfulvene was estimated in two ways: (1) by a method relying on the additivity of heat of sublimation values for the atoms in a hydrocarbon series,[6] and (2) by comparing the heats of sublimation of five hydrocarbons of nearly the same molecular weight as diphenylfulvene which have comparable structures. These estimates lead to a value lying between 23.5 and 26.1 kcal./mole. An intermediate value of 25 kcal./mole was arbitrarily selected.

The resonance contribution of the fulvene moiety of the diphenylfulvene can be estimated by subtracting the resonance energies of two phenyl groups from the total resonance energy of diphenylfulvene. This gives a value of 12.6 kcal./mole for the fulvene part. The good agreement between the resonance values of dimethylfulvene and the fulvene moiety in diphenylfulvene is no doubt to some extent fortuitous. Since the calculation of resonance energies from heats of combustion and from tables of bond values are subject to a number of uncertainties, such that resonance energies of the order of three or four kcal./mole may or may not be real, we feel justified only in the following conclusions: that the resonance energy of the fulvene moiety is large enough to be real, is about one-third that of benzene, and is roughly half way between that of cyclopentadiene and that of such rings as thiophene and furan. It is interesting that one calculation of the resonance energy of fulvene gives a value of about 11 kcal./mole.[7]

The values reported here are consistent with the

---

(5) G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley and Sons, New York, 1955, pp. 86–105.

(6) V. Tateveskii, *Doklady Akad. Nauk. S.S.S.R.*, **75**, 819 (1950); [*Chem. Abstr.*, **45**, 6038c (1951)].

(7) G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941).

little that is known of the chemistry of the simple fulvenes, since they behave like aliphatic compounds with some aromatic properties. They undergo the Diels-Alder reaction either as a diene or as a dienophile, they hydrogenate more like aliphatics than aromatics, and certain of them can undergo either addition or substitution under the proper conditions.[8] The effects on the fulvene moiety of substituents on the exo-cyclic carbon atom probably have little to do with the resonance of the fulvene part, since the ultraviolet and visible spectra of fulvene itself are virtually identical with those of the aliphatic substituted fulvenes.[9] The resonance of the fulvene part extends little or not at all beyond the exo-cyclic carbon atom, since even methyl groups suffer some steric effects and larger groups are tightly packed and restricted, judging from Fischer-Hirshfelder models. In diphenylfulvene the crowding is so great that it is hard to imagine any reasonable excited state which could achieve the required planarity between any two of the three rings. We feel this is ample justification in calculating the resonance energy of the fulvene part of diphenylfulvene by subtracting the energy of two isolated benzene rings (or by subtracting the resonance energy of benzophenone) from that of the whole molecule.

There is no doubt that fulvenes have some aromatic character. The aromatic sextet of electrons usually associated with five or six member aromatic rings can be written for fulvene if we allow one of the sextet to be written outside the ring. Fulvenes have a dipole moment of consequence,[10,11] with the ring negative and the exo-cyclic carbon atom positive. The outside electron is thus not really totally outside, and from this consideration alone one might predict as a first approximation that fulvene would be somewhat aromatic, but not as strongly so as structures which include the entire aromatic sextet within the ring. This interpretation is at least in accord with the facts.

It would be of great interest to determine the resonance energy of these fulvenes from heats of hydrogenation, since these data are subject to smaller uncertainty than heats of combustion. Bond distances from x-ray or electron diffraction studies would also be very welcome.

We are pleased to acknowledge the generous financial support of the Socony-Mobil Oil Co.

EXPERIMENTAL

The heats of combustion were determined using a series 1200 Parr oxygen bomb calorimeter, with a platinum combustion cup. The calorimeter was calibrated under the conditions of use with benzoic acid tablets standardized by the National Bureau of Standards. Parr calibrated mercury thermometers were used.

Dimethylfulvene was made by the usual method,[3] but with cooling of the reaction flask and attachment of a reflux condenser to minimize loss of cyclopentadiene. The product was steam distilled, the oil layer dried over Drierite, then distilled through a 34-plate column, b.p. 40° at 4 mm. Hg. Only the center cut from each distillation was used, and combustion runs were made only on freshly distilled product. The liquid sample was enclosed in a gelatin capsule for weighing and for combustion.

The diphenylfulvene was prepared in the usual manner,[3] and recrystallized from methyl alcohol several times until the melting point was not improved by further recrystallization; m.p. 81.5–81.7°. The recrystallization was done by cooling a warm saturated solution. A hot solution results in the formation of a precipitate, which is probably an oxidation product.[12] The final product was dried *in vacuo* at 25°. Further estimates of purity were made by adding various amounts of the most likely impurity, benzophenone, to the purified diphenylfulvene and noting the melting point depression and the increase in melting point range thus caused. By extrapolation on a graph of melting point depression *versus* melting point, the maximum amount of benzophenone impurity in the purified diphenylfulvene was calculated to be less than 0.2%. Spectra of the purified diphenylfulvene, by itself and with known added amounts of benzophenone, were run. From these data the maximum amount of benzophenone present was estimated to be less than 0.1%. The diphenylfulvene was pressed into pellets for weighing and combustion.

Analysis of spectral data was made on a Beckmann DU Spectrophotometer.

ATHENS, OHIO

---

[8] J. H. Day and C. Pidwerbesky, *J. Org. Chem.*, **20**, 89 (1955).

[9] J. Thiec and J. Wiemann, *Bull. soc. chim. France*, 177 (1956).

[10] G. W. Wheland, and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

[11] E. D. Bergman, and E. Fisher, *Bull. soc. chim. France*, **17**, 1084 (1950).

[12] C. Engler, *Z. Elektrochem.*, **18**, 945 (1912).