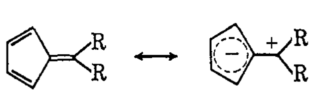
6,6-Dicyclopropylfulvene

ROBERT C. KERBER AND HAROLD G. LINDE, JR.

Department of Chemistry,
State University of New York at Stony Brook,
Stony Brook, Long Island, New York 11790

Received August 1, 1966

The fulvenes (I) are an interesting class of organic compounds, isomeric with benzenes, but with properties intermediate between those of aromatic and olefinic substances. The contribution of the "aromatic" dipolar resonance form to the ground state of the molecule is increased by substitution of electron-donating groups on the *exo* (6) carbon atom. This results in increased chemical stability, and physical properties more characteristic of an aromatic molecule.[1]



Ia, R = cyclo-C_3H_5
b, R = i-C_3H_7
c, R = CH_3
d, R = C_6H_5

The ability of cyclopropyl groups to stabilize carbonium ions is well documented,[2] and it seemed likely that substitution of cyclopropyl groups in the electron-deficient 6 position would similarly stabilize the fulvene molecule by augmenting the contribution of the dipolar resonance form.[3] Consequently, this study of 6,6-dicyclopropylfulvene (Ia) and its physical and chemical properties was undertaken.

Compound Ia was conveniently prepared by condensation of dicyclopropyl ketone and cyclopentadiene, using ethanolic sodium ethoxide.[3] 6,6-Diisopropylfulvene (Ib), intended for use as a reference compound, could not be obtained in significant yield by the same method, nor by use of potassium *t*-butoxide in *t*-butyl alcohol.[4] The use of 40% aqueous methylamine as a condensing agent, which was very successful for 6,6-dimethylfulvene[5] (Ic), failed in both of the above cases.

Dicyclopropylfulvene (Ia) was obtained as a deep yellow-orange liquid, which rather readily reacted with oxygen at room temperature. It could be stored for a few days at 0° in the absence of oxygen, or indefinitely at −78°.

The electronic spectrum of Ia in isooctane shows an intense absorption at 289 mμ (ϵ 1.93 × 10^4) and a weaker absorption at 365 mμ (ϵ 312). Dimethylfulvene (Ic), by comparison, absorbs at 265 mμ (ϵ 1.4 × 10^4) and 360 mμ (ϵ 317). The slightly longer wavelength absorption of Ia clearly reflects somewhat enhanced conjugation owing to the cyclopropyl groups.

A strong sharp band appears in the double-bond region of the infrared spectra of fulvenes.[6,7] It is generally assigned as the stretching frequency of the exocyclic C=C bond.[7] As can be seen from Table I, this band is quite sensitive to the 6 substituents; it changes in a manner consistent with the expectation that increasing electron-donating ability of R will (by favoring the dipolar resonance contributor) lower the bond order of the exocyclic bond, and therefore lower the stretching frequency.[8] The cyclopropyl group clearly shows an effect substantially beyond that of the ordinary aliphatic groups; in fact, it approaches phenyl in its effect on the C=C frequency. On the basis of the above argument, therefore, one can conclude that the cyclopropyl group is about as effective as a phenyl group at electron donation into the cyclopentadienyl ring of the fulvene.

TABLE I

EFFECT OF R IN  ON EXOCYCLIC C=C FREQUENCY (CCl_4 SOLUTIONS)

R	$\nu_{C=C}$, cm^{-1}	Ref
CH_3	1652, 1646, 1642	This work[a,b]
CH_3CH_2	1638	*a*
	1608, 1610	This work[c]
C_6H_5	1597, 1597	This work[b]
$(CH_3)_2N$	*ca.* 1550	*d*

[a] Reference 6. [b] References 7 and 8. [c] Reference 3. [d] K. Hartke, *Tetrahedron Letters*, 2737 (1964).

The proton magnetic resonance spectrum of neat Ia shows a symmetrical $A_2'B_2'$ pattern in the region τ 3.35–3.75 (area 3.9) owing to the "vinyl" protons, a multiplet at 8.1–8.6 (area 2.2) owing to the α-cyclopropyl protons, and a multiplet at 9.1–9.4 (area 8.0) corresponding to the β-cyclopropyl protons.[9] The "vinyl" pattern was very similar to that of diphenylfulvene (Id). The resonance of the 1 and 4 protons is centered about τ 3.65; that of the 2 and 3 protons is centered about 3.45. (For Id, the comparable resonances fall at τ 3.68 and 3.43.) Of greater relevance to the question of electron delocalization in Ia is the chemical shifts of the cyclopropyl protons (see Table II).

It is evident that the protons of the cyclopropyl rings of Ia are deshielded relative to those of 1,1-dicyclopropylethylene. This downfield shift provides further evidence of electron release from the cyclopropyl rings, since the chemical shifts of these protons are sensitive to electron deficiency.[2,10a] Comparison with the chemical shifts of dicyclopropylcarbonium ion suggests that the contribution of the dipolar resonance form is not overwhelming, but is nonetheless substantial.

---

[1] For a recent review, see K. Hafner, *et al.*, *Angew Chem. Intern. Ed. Engl.*, **2**, 123 (1963).

[2] See, for example, N. C. Deno, *et al.*, *J. Am. Chem. Soc.*, **87**, 4533 (1965); and C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965), and references therein.

[3] 6,6-Dicyclopropylfulvene (Ia) has recently been reported by M. Hanack and H. Eggensperger, *Ann.*, **663**, 31 (1963). However, little was reported concerning its chemical or physical properties.

[4] No fulvenes having two secondary alkyl groups in the 6 position are reported to date.

[5] W. Freiesleben, *Angew. Chem. Intern. Ed. Engl.*, **2**, 396 (1963).

[6] For several examples, see D. Meuche, *Helv. Chim. Acta*, **49**, 1279 (1966).

[7] J. C. Wood, R. M. Elofson, and D. M. Saunders, *Anal. Chem.*, **30**, 1339 (1958).

[8] That the trend in Table I is not primarily due to a ponderal effect is shown by the work of J. H. Day and R. Jenkins, *J. Org. Chem.*, **23**, 2039 (1958). These workers showed that a series of disubstituted fulvenes having alkyl groups of from two to eight carbons substituted in the 6 position all showed a strong C=C absorption in the range 1640–1647 cm^{-1}.

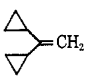
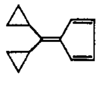
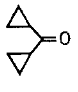
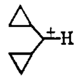
[9] In contrast to dimethyl- and dibenzylfulvenes,[10] substantially the same spectrum is observed in carbon tetrachloride, chloroform-d, and dimethyl sulfoxide solutions of Ia.

[10] W. B. Smith and B. A. Shoulders, *J. Am. Chem. Soc.*, **86**, 3118 (1964).

[10a] NOTE ADDED IN PROOF.—This argument neglects anisotropic effects owing to direct interaction between the β-cyclopropyl protons and the five-membered ring. That such effects may play a role is suggested by the nmr of dicyclopropylphenylcarbonium ion, which shows cyclopropyl resonances at τ 6.7–7.0 and 7.15–7.55.[2] Although the α protons are slightly less deshielded than in the dicyclopropyl carbonium ion, the β protons are more deshielded, owing possibly to proximity to the aromatic ring.

TABLE II

CHEMICAL SHIFTS OF CYCLOPROPYL PROTON MULTIPLETS (τ)

	α-H	β-H	Ref
	8.5–9.0	9.35–9.65	*a*
	8.08–8.60	9.08–9.41	This work
	7.69–8.18	8.92–9.33	This work
	6.5–7.1	7.2–7.7	*b*

[a] A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965). [b] N. Deno, *et al.*, *J. Am. Chem. Soc.*, **87**, 3000 (1965).

The most direct evidence of the enhanced contribution of the dipolar resonance form in Ia lies in the dipole moments of Ia and Ic. In dilute carbon tetrachloride solution at 20°, Ia has a dipole moment of 1.74 ± 0.05 D.; that of Ic is 1.52 ± 0.05 D.[11] This dipole moment is the highest reported for any fulvene containing only hydrocarbon groups. It unequivocally demonstrates the ability of the cyclopropyl ring to facilitate charge separation in a neutral molecule by stabilizing an electron-deficient center.

The stabilization of the fulvene molecule by the cyclopropyl groups, which is evident from the physical properties, is less evident from the chemical properties. Thus, Ia reacts readily with oxygen, as other fulvenes do, and reacts as a diene in the Diels–Alder reaction with maleic anhydride.[3] However, although reaction of Ic with maleic anhydride in refluxing benzene is essentially complete in 5 min as shown by loss of the yellow fulvene color, the reaction of Ia requires 2 to 3 hr under the same conditions.

Experimental Section

6,6-Dicyclopropylfulvene (Ia).—Freshly cut sodium metal (7.6 g, 0.33 g-atom) was dissolved in 125 ml of absolute ethanol, then 39.0 g (0.35 mole) of dicyclopropyl ketone (Aldrich Chemical Co.) was added. Freshly distilled cyclopentadiene was then added slowly in order to keep the temperature at or below 40°. After stirring overnight, the mixture was steam distilled until the distillate was nearly white. The nonaqueous layer was combined with methylene chloride washes of the aqueous layer, dried, and fractionated through a 12-in. spinning-band column. This yielded 7.0 g (13%) of dicyclopropylfulvene, bp 130–134° (18 mm), [lit.[3] bp 121–123° (13 mm)].[12] Samples for spectra and dipole moment studies were prepared by vpc, using a 10 ft × $^3/_8$ in. SF-96 on Chromosorb W column, in an Aerograph Model 700 Autoprep. Carbon–hydrogen analyses were invariably low, owing presumably to reaction with oxygen.[10]

The pure fulvene showed n^{20}_D 1.6005. On standing in air, the refractive index fell, and eventually a colorless precipitate formed, which showed broad bands at 3450 and 1720 cm^{-1} in the infrared (Nujol mull) and which did not melt below 200°.

6,6-Dimethylfulvene (Ic).—This compound was prepared by the method of Freiesleben[5] in 46% yield, bp 54–55.5° (17 mm), n^{25}_D 1.5416 [lit.[7] n^{25}_D 1.5404, bp 52° (10 mm)].

Attempts to make 6,6-diisopropylfulvene (Ib) by both the above methods failed. A preparation using diisopropyl ketone and cyclopentadiene in *t*-butyl alcohol containing potassium *t*-butoxide yielded on distillation a small amount of yellow material having an absorption maximum at 363 mμ in isooctane. No further work was done with this material.

Spectra.—Ultraviolet–visible spectra were obtained using a Perkin-Elmer Model 202 or a Carey Model 14 spectrophotometer. Infrared spectra were obtained in dilute carbon tetrachloride solutions, using a 0.1-mm cell in a Perkin-Elmer Infracord Model 137B, calibrated with a polystyrene film. Proton magnetic resonance spectra were obtained on a Varian A-60 spectrometer; chemical shifts are τ values relative to tetramethylsilane as internal standard (τ 10.00).

Dipole Moments.—These were determined from the dielectric constant of dilute carbon tetrachloride solutions at 20.0°, using a WTW dipolmeter, Model DM 01, obtained from Kahl Scientific Instrument Corp., El Cajon, Calif. The dipole moment was calculated by the method of Shoemaker and Garland,[13] using the following data: For Ia, $a(d\epsilon/dx_2)$ 3.944, $b(d\rho/dx_2)$ -1.824, n^{20}_D 1.6005, ρ_2 0.88 (assumed); for Ic a 2.930, b -1.034, n^{20}_D 1.5436, ρ_2 0.88.[14] These data yield for Ia $P_{2m^\circ} = 124.56$, $P_{2\mu^\circ} = 63.03$, $\mu = 1.74 \pm 0.05$ D; for Ic $P_{2m^\circ} = 86.20$, $P_{2\mu^\circ} = 48.13$, $\mu = 1.52 \pm 0.05$ D. All symbols are used as in ref 13.

Reactions with Maleic Anhydride.—Maleic anhydride (1.00 g, 10.2 mmoles) and 1.00 g of Ic (9.43 mmoles) were refluxed in 5 ml of benzene for 15 min (the yellow color was substantially discharged within 5 min), and the solution was evaporated. The residue was recrystallized from ether, then carbon tetrachloride–chloroform to give 0.80 g (40%) of white prisms, mp 137–138° (lit.[15] *exo* adduct mp 139–140°).

The same reaction, using 1.50 g (9.44 mmoles) of Ia for 3 hr gave a yellow residue from which a small amount of adduct, mp 120–122°, could be obtained by recrystallization from methanol (lit.[3] mp 120–122°).

Acknowledgments.—We wish to thank Mr. Norman Rapino for determining the dipole moment of Ic. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of the work, under Grant No. 562-Gl.

---

[11] G. W. Wheland and D. E. Mann [*J. Chem. Phys.*, **17**, 264 (1949)] reported a value of 1.48 ± 0.03 D. in benzene.

[12] That this boiling point is somewhat higher than might be expected from those of closely related compounds [6,6-dipropylfulvene, bp 92–93° (10 mm): *cf.* B. A. Kazanskii and F. N. Gakhanov, *Dokl. Akad. Nauk SSSR*, **64**, 521 (1949); *Chem. Abstr.*, **43**, 5370 (1949)] [6,6-hexamethylenefulvene, bp 81–82° (4 mm): *cf.* S. I. Khromov, E. S. Balenkova, and E. G. Treshchova, *Vestn. Mosk. Univ.*, **14**, 143 (1959); *Chem. Abstr.*, **54**, 9798] probably reflects greater intermolecular association owing to more polar ground state of Ia.

(13) D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 275–283.

(14) J. H. Day, *Chem. Rev.*, **53**, 167 (1953).

(15) D. Craig, *et al.*, *J. Am. Chem. Soc.*, **76**, 4573 (1954).

The Methylation of 1,2-Diarylethylenes by Dimethylsulfinyl Carbanion

M. FELDMAN, S. DANISHEFSKY, AND R. LEVINE

Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania 15213

Received July 25, 1966

Recent reports of the ability of dimethylsulfinyl carbanion (DMSO$^-$) to methylate various unsaturated systems,[1–3] prompt us to disclose our findings which may be of relevance to the mechanism of these reactions. In the course of other studies we had occasion to treat certain 1,2-diarylethylenes with DMSO$^-$.

---

(1) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965).

(2) G. A. Russel and S. A. Weiner, *ibid.*, **31**, 248 (1966).

(3) H. Noyaki, Y. Yamamoto, and R. Noyori, *Tetrahedron Letters*, 1123 (1966).