Figure 1. Plot of methyl hfsc $vs.$ σ. Ordinate: methyl hfsc, uncertainties are average deviations; abscissa: σ, uncertainties are estimates of McDaniel and Brown (uncertainties of $\sigma_m{}^- {}_{-o}$ and $\sigma^-{}_{p-CN}$ are arbitrary). Circle indicates $\sigma^-{}_{p-CN}$ point.

coefficient between σ and nitrogen hfsc for those substituents in common, omitting anomalous substituents, is 0.942 (seven values) for nitrobenzene anion radicals in aqueous acetone[1] and 0.778 (six values) for phenyl t-butyl nitroxides in $(CH_2OH)_2$.[2] The methyl hfsc also

Table I. Methyl Hfsc for Substituted 1-Phenyl-1,2-propanesemidiones

Substituent	$A^H{}_{Me}$	σ
p-CN	2.18	0.66 ($\sigma - =$ 1.00[a])
p-CF$_3$	2.67	0.54
m-CN	2.82	0.56
m-CF$_3$	3.02	0.43
m-Br	3.03	0.391
m-Cl	3.05	0.373
m-F	3.10	0.337
p-Ph	3.14	−0.01
p-Br	3.15	0.232
p-Cl	3.22	0.227
m-OCH$_3$	3.39	0.115
p-H	3.43	0.000
m-CH$_3$	3.52	−0.069
p-F	3.59	0.062
m-NH$_2$	3.60	−0.16
p-CH$_3$	3.63	−0.170
p-C(CH$_3$)$_3$	3.65	−0.197
p-OCH$_3$	3.88	−0.268
p-N(CH$_3$)$_2$	4.12	−0.83
p-NH$_2$	4.30	−0.66
m-O$^-$	4.33	−0.708[a]

[a] Taken from H. H. Jaffe, Chem. Rev., 53, 191 (1953).

show far greater variation with substituent than do the nitrogen hfsc. The ρ values for methyl splittings, nitrogen splittings in nitrobenzene radicals,[1] and nitrogen splittings in nitroxides[2] are −0.84, −0.30,[9a] and −0.39,[9b] respectively.

The excellent correlation with σ for the "well-behaved" substituents may in part be due to the fact that σ constants derived from ionization constants of benzoic acids measure a substituent effect on electron density at an atom β to the benzene ring as do the methyl hfsc. The deviations of p-F, p-Ph, p-CF$_3$, and p-CN may indicate that these substituents have different effects on unpaired and paired electron density.[10] The p-F group is also anomalous in promoting the rearrangement of 2-methyl-2-phenyl-1-propyl radicals.[11] The normal behavior of m-F indicates the anomaly stems from resonance interactions involving the p electrons. Unpublished work of Janzen demonstrates that hfsc within a series better correlate for −R groups with σ^- than σ.[12] The plot shows, accordingly, that the σ^- point for p-CN is quite close to the least-squares line.

The deviation of p-N(CH$_3$)$_2$ possibly stems from experimental uncertainty in the σ constant, due to the difficulty in correcting for zwitterion. The value for this substituent taken from Jaffe's compilation,[13] −0.600, fits reasonably well with the other data.

Other radicals which should give good correlations with σ are substituted monaryl nitroxides (the -NH splitting) and radical anions of substituted acetophenones, benzaldehydes, and phenylglyoxals (the -CH and -CCH$_3$ splittings). Additional data may reveal the necessity of a new set of σ constants, $\sigma^-\cdot$, necessary to correlate one electron delocalization. Work is in progress in this area.[13a]

Acknowledgment. The author is very grateful to Mr. R. Petkun for synthesis of many of the starting materials and to Drs. J. Weinstein and E. G. Janzen for helpful discussions.

(9) Calculated omitting anomalous substituents: (a) 17 values; (b) 13 values. The Figure 1 x-axis direction is opposite to that used in the calculation.

(10) See A. Streitwieser, Jr., and C. Perrin, J. Am. Chem. Soc., 86, 4938 (1964); B. D. Gilliom and B. E. Wood, ibid., 87, 3944 (1965).

(11) C. Ruchardt and S. Eichler, Ber., 95, 1921 (1962).

(12) Private communication from E. G. Janzen.

(13) H. H. Jaffe, Chem. Rev., 53, 191 (1953).

(13a) NOTE ADDED IN PROOF. The substituent parameter for p-CF$_3$ measured from the ionization of anilinium ions, 0.65 (W. A. Sheppard, J. Am. Chem. Soc., 87, 2410 (1965)), puts this group on the correlation line. This could be interpreted as additional evidence for fluorine 1,3 p–π conjugation.

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A Photochemical 1,3 Cycloaddition of Olefins to Benzene[1]

Sir:

We wish to report a photochemical cycloaddition of olefins to benzene different from that recently reported[2] by Srinivasan and Hill for cyclobutene. We find that the adducts from cis-but-2-ene (Ib), cyclopentene (Ic), and 2,3-dimethylbut-2-ene (Id) are substituted tricyclo-[5.1.0.^{4,8}]oct-2-enes (I). They correspond to addition of an olefin across a cyclopropyl ring of benzvalene (II).

The photochemical formation of a benzvalene from a benzene homolog has been reported.[3] The mode of addition resembles the 1,3 cycloaddition observed in the photodimerization of butadiene to a bicyclo[3.1.0]-hexane.[4]
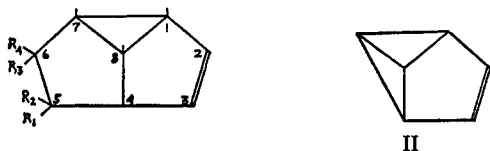
Ia, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
c, $R_2 = R_4 = H$; R_1, $R_3 = -(CH_2)_3-$
d, $R_1 = R_2 = R_3 = R_4 = CH_3$

The adducts are formed[5] by irradiation of solutions ($\sim 10\%$) of the olefins in benzene, at room temperature under nitrogen, with light of 2537 A (Hg resonance lamp, Corning 7910 filter). They can be separated by gas chromatography[6] from other hydrocarbon products. Their mass spectral molecular weights[7] show them to be 1:1 adducts of olefin and benzene. All three have absorption maxima at 220 mμ ($\epsilon \sim 3000$). Ib and Ic exhibit strong absorptions at 3.28, 3.40, and 3.48 μ in the C–H stretching region and moderate absorption at 6.24 μ in the C=C region. The presence of the ultraviolet maxima in hydrocarbons having only one double bond (vide infra) is difficult to explain except on the basis of a vinylcyclopropane chromophore.[8] The C–H stretching vibrations, although not typical of simple cyclopropanes, are strikingly similar to those of tricyclo[5.1.0.0^{4,8}]oct-2-ene (Ia), as reported[9] by Chapman, et al.

Additional evidence that the adducts are derivatives of Ia is provided by their 100 Mc nmr spectra.[10] That of the butene adduct (Ib) is shown in Figure 1. The spectrum shows two methyl groups as doublets at high field, indicating that each is attached to a saturated carbon atom bearing one hydrogen, and suggesting that the butene moiety is intact. By double resonance, these methine protons are located in the three-proton area centered at τ 7.45. The six obviously unique protons derived from benzene thus fall at τ 4.42, 4.52, 7.17, $\sim$7.45, 8.25, and 8.38. The spectrum of the dimethylbutene adduct (Id) shows six unique protons with corresponding chemical shifts, two methyl groups at τ 9.05, and two methyl groups as singlets at τ 9.15 and 9.36. The spectrum of the cyclopentene adduct (Ic) shows two nonequivalent protons at τ 4.39 and 4.46, an area of four protons from τ 6.6 to 7.4, and an area of eight protons from τ 8.15 to 8.75. By using perdeuterated benzene, it was possible to locate the ben-
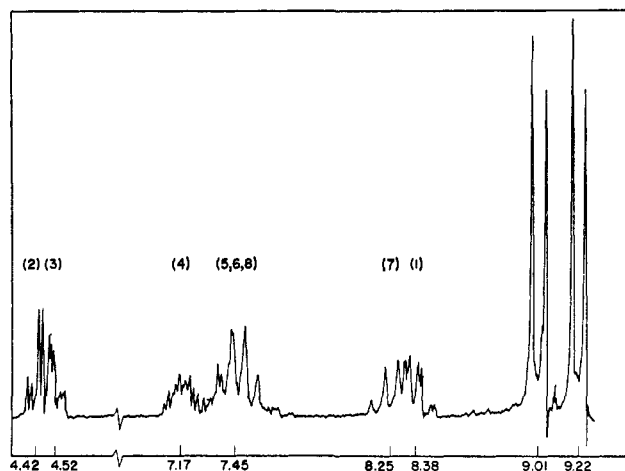

Figure 1. 100 Mc nmr spectrum of 5,6-dimethyltricyclo[5.1.0.0^{4,8}]-oct-2-ene (Ib). Abscissae are τ values. Numbers in parentheses relate to positions of protons in structure Ib.

zene protons and show that their chemical shifts correspond closely to those of Ib.

In all three adducts the strong coupling ($J = 5.2$–5.5 cps) between the olefinic protons ($\tau \sim 4.5$) indicates the presence of only one double bond. The butene and dimethylbutene adducts must thus be tricyclic, the cyclopentene adduct tetracyclic. The chemical shifts, as well as the coupling constants, of the olefinic protons are in accord with expectations for vinyl protons in a cyclopentene ring and markedly resemble those of Ia.[9]

Decoupling experiments, particularly on Ib, lead to an unambiguous assignment of structure. In each of the three adducts, one olefinic proton is coupled to a proton at high field while the other is coupled to one at intermediate field; in Ib, $J_{1,2} \simeq J_{3,4} = 2$ cps. In adducts Ib and Id, where the high-field benzene protons are not obscured, these protons are strongly coupled (7 cps) to each other and each is strongly coupled to a proton near τ 7.5. Since the latter must be a benzene proton in the case of Id, it is reasonable to conclude that it is also a benzene proton in Ib. In Ib one of the benzene protons at high field (7) is strongly coupled (6 cps) to a second (hence a butene) proton in the τ 7.45 group; another benzene proton (4) is also coupled (5 cps) to two protons in this group. If the butene moiety is intact, it must be concluded that protons 1, 7, and 4 are each coupled to the benzene proton at τ 7.45 and that protons 4 and 7 are coupled to different butene protons. The butene adduct must therefore be 5,6-dimethyltricyclo[5.1.0.0^{4,8}]oct-2-ene (Ib);[11] the cyclopentene and dimethylbutene adducts must have analogous structures.[12]

(3) K. E. Wilzbach and L. Kaplan, J. Am. Chem. Soc., 87, 4004 (1965).
(4) R. Srinivasan and F. I. Sonntag, ibid., 87, 3778 (1965).
(5) Initial quantum yields for formation of Ib and Ic are about 0.04; that for Id about 0.005.
(6) Ib and Ic are the major products from their respective irradiations; the yield of Id is exceeded by that of another 1:1 adduct, probably monocyclic. Retention volumes on Carbowax 20M (Chromosorb G support) at 80° relative to durene: Ib, 0.33; Ic, 1.40; Id, 0.54.
(7) We thank Lee Harkness for these determinations.
(8) W. G. Dauben and G. J. Fonken, J. Am. Chem. Soc., 81, 4060 (1959). Cf. ref 9, footnote 10.
(9) O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, ibid., 86, 2660 (1964).
(10) Spectra taken in CCl₄ solution with internal TMS reference on Varian HA-100 spectrometer. We thank Miss Gail Norman for these measurements.

(11) Four stereoisomers of this structure are possible. The strong coupling of protons 4 and 7 to the butene protons suggests that the cis configuration of the butene moiety has been retained and that the methyl groups are endo.
(12) NOTE ADDED IN PROOF. (a) In conformity with IUPAC rules for naming polycyclic systems, as discussed by J. Meinwald and J. K. Crandall, J. Am. Chem. Soc., 88, 1292 (1966), the adducts should be named as tricyclo[3.3.0.0^{2,8}]oct-3-enes, substituted at positions 6 and 7. (b) Dr. R. Srinivasan has asked us to add in proof the statement that "the photochemical addition of benzene to cyclobutene also leads to a second product which is similar in structure to the adducts formed by 2-butene and cyclopentene with benzene."

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Communications to the Editor