Table I. Calculation of $\sigma_R{}^0$ Values from the Integrated Intensities (A) of the ν_{16} Bands in Monosubstituted Benzenes

Substituent	$A^{1/2a}$	$\pm\sigma_R{}^0$ (calcd.)	$-\sigma_R{}^0$ (n.m.r.)[c]	$-\sigma_R{}^0$ (reactivity)[c]	$\bar\sigma_R$ (n.m.r.)[d]	$\bar\sigma_R$ (reactivity)[f]
NMe₂	71.4	0.53	0.54	0.52	...	...
OMe	57.7	0.425	0.43	0.41	...	...
OH	54.2	0.40	0.43	0.40	...	...
F	46.4	0.345	0.32	0.35	...	...
OCOMe	32.7	0.24	0.21	...	...	...
Br	32.3	0.24	0.163	0.19	...	...
Cl	30.5	0.225	0.18	0.20	...	...
COMe	30.7[b]	0.225[b]	...	...	0.19	0.12
CO₂Et	25.9[b]	0.19[b]	...	...	0.195	0.08
NO₂	25.2	0.185	...	...	0.19	0.14
CF₃	17.8	0.135	...	...	0.10[e]	0.02
Et	17.0	0.125	0.14	0.09	...	...
Me	16.6	0.125	0.146	0.10	...	...
CN	15.1	0.11	...	...	0.21	0.08
CH₂Cl	9.5	0.07	0.03	...	...	...
CCl₃	0	0.00	...	...	...	...

[a] Precision better than ±1 $(A$ in l. mole⁻¹ cm.⁻²). [b] May be exalted; see text. [c] Reference 2. [d] Reference 2; calculated from figures for dilute solutions in cyclohexane using the formula given therein. [e] Calculated from figures in L. M. Yagupol'ski, V. F. Bystrov, A. V. Stepanyants, and Yu. A. Fialkov, *Zh. Obshch. Khim.*, **34**, 3682 (1964). [f] Values are $2.0\sigma_R{}^m$: R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

rings which appear at about 1600 and 1585 cm.⁻¹ (ν_{16a} and ν_{16b} using Herzberg's notation) should be a function of the charge disturbance in the ring. An approximate relationship between the apparent extinction coefficients of these bands for monosubstituted benzenes and the mesomeric moments of the substituents was shown at that time. We now find that the square roots of the total integrated areas of these absorption bands correlate closely with reported $\sigma_R{}^0$ values. Figure 1 shows the correlation with $\sigma_R{}^0$ for eight substituents for which such values were available[2] from both reactivity and n.m.r. measurements. That the rate of change of dipole moment with the normal coordinate at the equilibrium position $(\partial\mu/\partial Q)$, which is proportional to $A^{1/2}$, should be affected only by the resonance interaction of the substituent is reasonable as $\partial\mu/\partial Q$ for this vibration might be expected to be determined mainly by the π-electrons of the ring. The negligible influence of inductive effects is confirmed by the low intensity $(A < 2)$ of the vibration for benzotrichloride, which has a relatively high dipole moment. Further discussion of these matters is reserved for a forthcoming paper.

We have used the empirical equation, $\sigma_R{}^0 = 0.0074 \cdot A^{1/2}$, derived from the figure by inspection, to calculate values for a total of sixteen substituents, and these values are compared with previously reported $\sigma_R{}^0$ and $\bar\sigma_R$ values in Table I.

The intensities were measured on a Perkin-Elmer 125 spectrometer using the solvent-compensation technique, the samples being made up as dilute solutions in carbon tetrachloride. The two ν_{16} bands were integrated together partly for convenience and partly because it is probably not valid to separate them if the substituent is not of C_{2v} or higher symmetry (as will be discussed in the full paper). The benzene derivatives were purified by standard techniques and their purity checked by gas chromatography.

The procedure offers a simple method of determining solvent and temperature effects on resonance interactions in monosubstituted benzenes. In addition, unlike the methods discussed above, it is potentially applicable to such interactions in more complex systems. We are currently investigating these matters using a range of mono- and disubstituted benzenes

and monosubstituted pyridines. Other skeletal modes are also being studied. The only limitations appear to be that no sign can be given to the $\sigma_R{}^0$ values in monosubstituted benzenes and that values for compounds
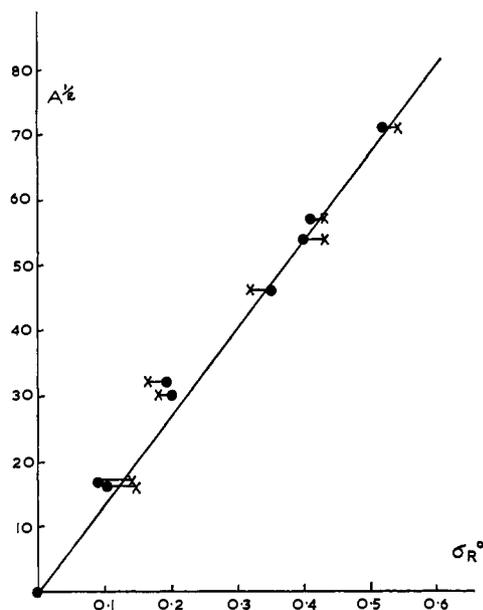
Figure 1. Plot of $A^{1/2}$ (A in l. mole⁻¹ cm.⁻²) *vs.* $\sigma_R{}^0$ values (reactivity, ●; fluorine n.m.r., ✕).

having another strong band near 1600 cm.⁻¹ (*e.g.*, those with an α carbonyl group) may be exalted by coupling.

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Photodimerization of Metal-Complexed Olefins

Sir:

We wish to report the first clear-cut example of a new type of dimerization reaction, the light-induced cycloaddition of olefins in the presence of certain metal
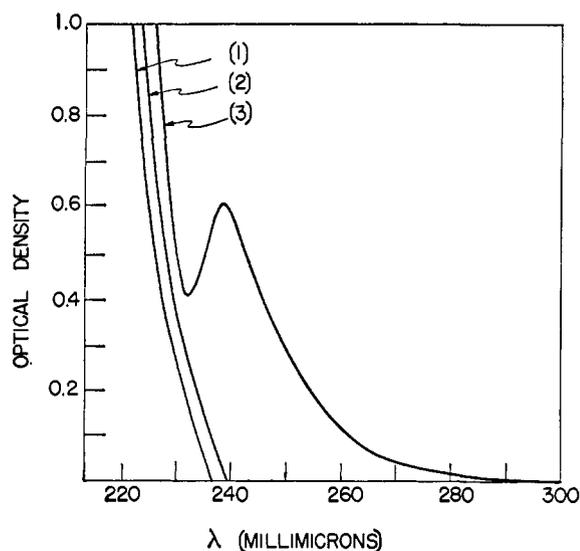
Figure 1. Ultraviolet spectra of (1) 7.6 × 10⁻⁴ M CuBr in ether, (2) 1.06 M norbornene in ether, and (3) 5.85 × 10⁻⁶ M CuBr and 5.3 × 10⁻² M norbornene in ether. Path length was 1 cm. in each case.

salts.[1] Norbornene, when irradiated[2] in a solution containing copper(I) halides, afforded the *exo,trans,exo* isomer of dodecahydro-1,4:5,8-dimethanobiphenylene (I).
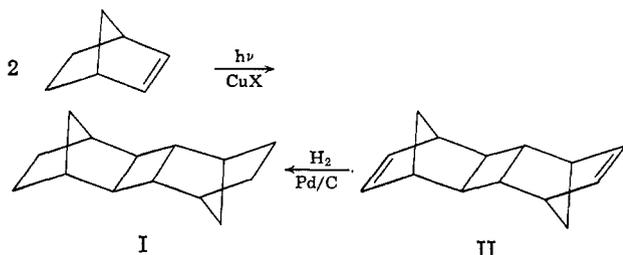
The reaction was facile and remarkably stereo-specific. In the dark no dimerization occurred. Irradiation in the absence of cuprous salts likewise afforded no dimer. Of the likely complex-forming metal systems, only the cuprous halides proved effective in preliminary experiments. Silver nitrate, tetrachloroauric(III) acid, dichlorobis(benzonitrile)palladium(II), platinum(II) chloride, dicobalt octacarbonyl, iron pentacarbonyl, rhodium(III) chloride, and bis(1,5-cyclooctadiene)nickel(0) failed to promote dimerization.

In a typical experiment, a solution of norbornene (450 g., 4.78 moles) in anhydrous ether (150 ml.) was stirred vigorously with cuprous bromide (4.0 g., 0.028 mole) under nitrogen and irradiated in a tubular reactor for 149 hr.[2] Distillation afforded *exo,trans,exo*-dodecahydro-1,4:5,8-dimethanobiphenylene (b.p. 95–96° (1.2 mm.), 115 g., 0.61 mole, 26% yield) as a clear liquid that crystallized immediately. Recrystallization from ethanol gave white needles that melted

at 64–64.5°. *Anal.* Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71; mol. wt., 188. Found: C, 89.37; H, 10.71; mol. wt., 187. This material was shown to be identical in every respect[3] with the hydrocarbon obtained from hydrogenation of *exo,trans,exo*-1,4,5,-8,9,10,11,12-octahydro-1,4:5,8-dimethanobiphenylene (II).[4] V.p.c. analysis of various reaction mixtures[5] established that I constituted 97% of the dimeric products; the *exo,trans,endo* isomer[6] accounted for the other 3%.

In contrast to the striking stereospecificity of this reaction, Scharf and Korte[7] and Arnold and co-workers[4] found that a distinct *mixture* of $C_{14}H_{20}$ dimers was obtained when norbornene was irradiated in the presence of photosensitizing agents. In such reactions, the *exo,trans endo* isomer, rather than the *exo,trans,exo* form, was found to be the major product.

The involvement of a copper halide–norbornene complex was indicated by spectral data. Ether solutions of norbornene or CuX separately gave no maximum in the ultraviolet beyond the ether cut-off at 220 mμ. A mixture of the two, however, gave rise to an intense absorption band at 239 mμ (Figure 1), suggesting a strong interaction between the metal and the olefinic double bond,[8] probably of the type depicted by Dewar[9] for silver(I)–ethylene. Irradiation of copper(I)–norbornene solutions in ether with 2537 Å. light, which is >99% selectively absorbed by the complex, readily afforded I. In the absence of the cuprous salt no dimerization occurred. The infrared spectrum of the isolated complex, prepared by the method of Haight, et al.,[10,11] and stored at −78°, had no absorption characteristic of the norbornene double bond (3050, 1653, and 707 cm.⁻¹)[12,13] and, in fact, closely resembled the spectrum of norbornane.

The photodimerization followed apparent zero-order kinetics up to 0.5% conversions over a range of norbornene concentrations. This is in accord with the facts that norbornene was always present in large excess and that the initial rates of excitation were directly dependent on light intensity and remained con-

(1) Certain formally analogous reactions have been reported; for example, the "bird cage" dimer of norbornadiene reportedly arises from either a thermal (dark) or light-induced reaction of norbornadiene with the complex, norbornadiene–iron tricarbonyl [D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 368 (1961); C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *ibid.*, 373 (1961)]. Intramolecular cyclization results when butadiene and 1,5-cyclooctadiene are irradiated in the presence of cuprous chloride [R. Srinivasan, *J. Am. Chem. Soc.*, 85, 3048 (1963); 86, 3318 (1964)].

(2) A 450-w. high-pressure mercury arc and Vycor optics were used in these experiments.

(3) Melting points, a mixture melting point, infrared and n.m.r. spectra, and v.p.c. retention times on a variety of columns were completely identical.

(4) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, 87, 2596 (1965).

(5) Dimerization proceeded equally well from either CuCl or CuBr. Higher yields of dimer were obtained when the lamp finger was cleaned daily and fresh batches of cuprous salts were added.

(6) An authentic sample was obtained from hydrogenation of the diene precursor[4] and from the acetophenone-sensitized photodimerization of norbornene.[4,7]

(7) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963).

(8) Norbornene is known to form complexes readily with silver salts. Cf. J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, 81, 571 (1959), and M. A. Muhs and F. T. Weiss, *ibid.*, 84, 4697 (1962).

(9) M. J. S. Dewar, *Bull. soc. chim. France*, 18, C79 (1951).

(10) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, 2, 1201 (1963).

(11) The complex analyzed roughly for $(C_7H_{10})_n(CuCl)_n$ (*Anal.* Found: C, 39.83; H, 4.98; Cu, 31.83; Cl, 19.55). The unstable nature of the complex prevented further purification.

(12) R. C. Lord and R. W. Walker, *J. Am. Chem. Soc.*, 76, 2518 (1954); P. R. Schleyer, *ibid.*, 80, 1700 (1958).

(13) The possibility exists that the norbornene =C—H band at 3050 cm.⁻¹ and the C=C band at 1653 cm.⁻¹ shifted downfield in the complex, as with similar norbornadiene–cuprous halide coordination compounds.[14,15] If so, such absorptions were masked in our spectrum by other peaks. It is clear, however, that the strong absorption at 707 cm.⁻¹ disappeared altogether.

(14) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(15) G. N. Schrauzer and S. Eichler, *Chem. Ber.*, 95, 260 (1962).

stant as long as sufficient complex was present to absorb all of the incident light. The several mechanistic pathways consonant with these findings cannot be distinguished without detailed quantum yield studies. Work to these ends is now underway.

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Synthesis of *meso*-, *rac*-, and (−)-(4R,6R)-2,4,6,8-Tetramethylnonane, the Simplest Low Molecular Weight Model Compounds of Isotactic and Syndiotactic Polypropylene

Sir:

No low molecular weight models of the two known[1,2] crystalline diastereoisomeric polypropylenes have been prepared up to now. We wish to report the preparation, the separation, and the identification of the two diaster-

The paraffin has been shown by v.p.c. (90-m. squalane capillary column)[5] to be a mixture of two components only, that having the larger retention time predominating (54%). The two components, separated by accurate rectification, controlling the composition of the 34 fractions by v.p.c., were in fact the two possible diastereoisomers of 2,4,6,8-tetramethylnonane as shown by identical elemental composition, molecular weight, and MR_D by different boiling and melting points (Table I), by infrared spectra that were practically identical in the C–H stretching region but remarkably different in the region between 1400 and 700 cm.$^{-1}$ (Figure 1), and by n.m.r.[6] spectra (Figure 2) which were different.

In order to establish which of the two diastereoisomers was the *meso* (isotactic, a) and which was the racemic (syndiotactic, b), the optically active mixture was prepared by the same method, starting with (+)(R)-2,6,8-trimethylnonan-4-one (II).

Compound II was prepared starting with 2,4-dimethylpentanoic acid which had been resolved as re-

Table I

Compound	B.p., °C. (mm.)	M.p., °C.	Analysis,[a] % C	H	Mol. wt.,[b] Found	$n^{25}D$	d_4^{25}	MR_D,[c] found
a[d]	82.5 (20)	−58 to −56	84.71	15.27	188	1.4192	0.7469	62.35
b[e]	85 (22)	−60 to −58	84.74	15.12	188	1.4187	0.7460	62.36

[a] Calcd. for $C_{13}H_{28}$: C, 84.69; H, 15.31. [b] Calcd. for $C_{13}H_{28}$: 184.36. [c] Calcd.: 62.40. [d] Steric purity ∼95%. [e] Steric purity >98%.

eoisomers of 2,4,6,8-tetramethylnonane, which is the simplest paraffin of the type $CH_3(CH(CH_3)CH_2)_nCH(CH_3)_2$ existing in two diastereoisomeric forms (shown in the Fischer projections a and b).
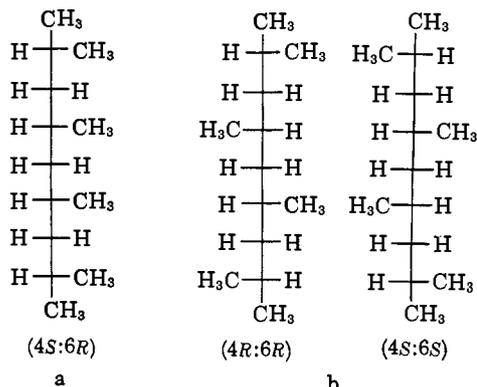
By allowing 2,6,8-trimethylnonan-4-one[3,4] to react with methylmagnesium bromide, 2,4,6,8-tetramethyl-nonan-4-ol (I), b.p. 110° (17 mm.), $n^{20}D$ 1.4393 (*Anal.* Found: C, 77.88; H, 13.88), has been obtained.

The alcohol on dehydration by rapid distillation in the presence of iodine gave a mixture of isomeric olefins which by hydrogenation (H_2) in the presence of Raney nickel at 120° yielded 2,4,6,8-tetramethylnonane. *Anal.* Found: C, 84.05; H, 15.15; mol. wt. (cryoscopic in benzene), 187.

(1) G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.*, 77, 1708 (1955).
(2) G. Natta, P. Pasquon, P. Corradini, M. Peraldo, M. Pegoraro, and A. Zambelli, *Rend. Acc. Naz. Lincei*, [VIII] 28, 539 (1960).
(3) F. Bodroux and F. Taboury, *Bull. soc. chim. France*, 5, 950 (1909).
(4) J. E. Dubois and M. Chastrette, *Tetrahedron Letters*, 32, 2229 (1964).

ported by Levene and Bass.[7] From a sample of acid having $[\alpha]^{20}D$ −8.42° (neat) (optical purity 40%[7]), by reduction with $LiAlH_4$ and reaction with PBr_3 (+)(R)-1-bromo-2,4-dimethylpentane[8] (III) was obtained; $[\alpha]^{20}D$ +2.91° (neat).

The Grignard compound prepared starting with III was treated with 3-methylbutanal, yielding (−)(6R)-2,6,8-trimethylnonan-4-ol, $[\alpha]^{20}D$ −1.14° (neat), which by chromic acid oxidation yielded II, $[\alpha]^{20}D$ +2.62° (neat).

The mixture of paraffins $\alpha^{17}D$ ($l = 1$) −1.92 ± 0.025° (neat, 1-dm.) which contained 46 ± 2% of the isomer with lower retention time yielded, by rectification, optically active fractions the composition of which was determined by v.p.c. (Perkin-Elmer Model F 11 vapor fractometer, 2-m. column of Apiezon L on Chromosorb P, flame ionization detector, 105°).

A plot of the rotation of the fractions measured in a microtube (accuracy of ±0.025°) against their composition is linear and extrapolates to $\alpha^{17}D$ +0.04 ± 0.05° (neat, 1 dm.)[9] for the lower boiling isomer, indicating that this isomer is the *meso* (isotactic) diastereoisomer (a) while the higher boiling diastereoisomer, which has $\alpha^{17}D$ ($l = 1$) −3.75 ± 0.05° (1 dm.)[9] and $[M]^{17}D$ (extrapolated to 100% optical purity) −23.0 ± 0.3°, in good agreement with the value calculated according to Brewster (−24°), is the R:R (syndiotactic) diastereoisomer (b).

(7) P. A. Levene and L. W. Bass, *J. Biol. Chem.*, 70, 217 (1926).
(8) P. A. Levene and R. E. Marker, *ibid.*, 111, 310 (1935).
(9) Standard deviation calculated by the least-squares method.