

Table I. Decarbonylation of Acyl Chlorides

Acyl chloride (g)	RhCl-(Ph <sub>3</sub> P) <sub>3</sub> , g	Solvent (ml)	Reaction		Products (%)	
			Temp	Time	Olefin, <sup>a</sup> chloride	RhCCOCl-(Ph <sub>3</sub> P) <sub>2</sub>
PhCH <sub>2</sub> COCl (0.5)	0.462	Benzene (10)	Reflux	10 min	PhCH <sub>2</sub> Cl (81)	(97)
PhCH <sub>2</sub> COCl (0.5)	0.462	CH <sub>2</sub> Cl <sub>2</sub> (10)	Room temp	1 days	PhCH <sub>2</sub> Cl (86)	(95)
PhCH <sub>2</sub> CH <sub>2</sub> COCl (0.5)	0.462	Toluene (10)	Reflux	30 min	PhCH=CH <sub>2</sub> (71)	(80)

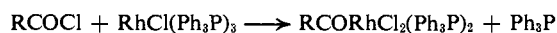
<sup>a</sup> The yield was determined by gas chromatography.

Table II. RCORhCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> Complex

R	Mp dec, °C	Mol wt		C		H		Cl		P	
		Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>	173-177	724	797	63.21	63.16	5.15	5.14	9.03	8.91	7.74	7.78
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub>	165-166	806	811	63.37	63.6	5.22	5.31	9.37	8.75	7.1	7.52
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub>	135-137	904	937	66.37	66.59	6.58	6.51	7.63	7.58	6.87	6.61
Cyclohexyl	167-169	...	...	64.57	63.90	5.15	5.25	8.31	8.79		

specific method of decarbonylation of acyl halides under mild conditions and seems to be useful in organic syntheses. Some experimental results are shown in Table I.

By careful investigation of the reaction between acyl halide and chlorotris(triphenylphosphine)rhodium, we have found that a new acylrhodium complex can be isolated in a good yield with elimination of 1 mole of triphenylphosphine under carefully controlled conditions.<sup>3</sup> Oxidative addition of acyl chloride to form a five-coordinated rhodium acyl complex appears to occur.



A number of complexes having acyl-metal bonds are known and are usually prepared by insertion of carbon monoxide into an alkyl-metal bond. Although the addition of covalent compounds to coordinately unsaturated metal compounds is a common reaction, this is the first example that an acyl complex is formed by the oxidative addition of acyl halide to a complex. Also this result indicates that an electrophilic attack on the rhodium by the carbonyl carbon is possible.

The following is a typical example. Chlorotris(triphenylphosphine)rhodium (9.24 g, 0.01 mole) was dissolved in anhydrous benzene (30 ml) and palmitoyl chloride (R = CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>; 3.02 g, 0.11 mole) was added under nitrogen. The mixture was refluxed for 20 min in an oil bath. The dark red color of the original mixture instantly turned orange-red. Most of the benzene was removed and hexane was added to the residue to give a pale brown solid (9.20 g, 99%). The solid was dissolved in benzene and reprecipitated with ethanol to give dichloropalmitoylbis(triphenylphosphine)rhodium. The complex showed a sharp infrared band at 1715 cm<sup>-1</sup> (acylrhodium carbonyl). The nmr spectrum showed a triplet at  $\tau$  7.08 (two protons, methylene protons next to the carbonyl). The following other peaks are consistent with the assigned structure:  $\tau$  2.34 (12 H), 2.58 (18 H), 8.69 (26 H), 9.09 (3 H). The complex is stable in air and does not react with water and alcohols.

(3) Recently, Wilkinson, *et al.*, reported the formation of an acylrhodium complex by carbonylating the ethylrhodium complex, without giving experimental details: M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966).

Other acyl chlorides formed the corresponding complexes, but the stability of the complexes is somewhat different depending on the structure of acyl chloride. Some complexes obtained are shown in Table II. Acetyl chloride and benzoyl chloride were exceptions. They gave CH<sub>3</sub>RhCOCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> and PhRhCOCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>, respectively, as reported by Wilkinson, *et al.*<sup>3</sup>

As expected, the complex gave rise to olefin, hydrogen chloride, and chlorocarbonylbis(triphenylphosphine)rhodium when heated. For example, the palmitoyl complex gave rise to *trans*-2-pentadecene, containing a small amount of isomeric pentadecenes. However, 1-pentadecene was selectively obtained when the complex was treated with an equivalent amount of iodine in chloroform at room temperature. By the reaction of carbon monoxide (50 kg/cm<sup>2</sup>) at room temperature with the acyl complex, the acyl chloride was recovered in a high yield.

The above results, combined with the Wilkinson's works, give very important clues to the mechanism of carbonylation and decarbonylation reactions catalyzed by noble metal compounds, which we will discuss elsewhere.

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## Bullvalene. Motion in the Solid

Sir:

Since the synthesis of bullvalene by Schröder and the confirmation<sup>1</sup> of the prediction by Doering and Roth<sup>2</sup> that at high temperatures the nmr spectrum in solution would consist of a single line, there has been much interest in organic molecules with fluctuating structures. Saunders<sup>3</sup> has measured the rate of rearrangement in bullvalene as a function of temperature by nmr as has Gutowsky<sup>4</sup> using a spin-echo nmr technique. The activation parameters which were determined in these two solution investigations are in agreement.

(1) G. Schröder, *Angew. Chem.*, **75**, 722 (1963).

(2) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).

(3) M. Saunders, *Tetrahedron Letters*, 1699 (1963).

(4) A. Allerhand and H. S. Gutowsky, *J. Am. Chem. Soc.*, **87**, 4092 (1965).

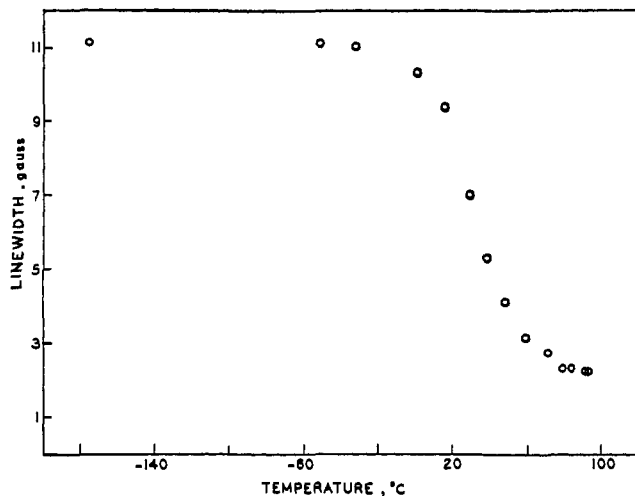


Figure 1. Line width as a function of temperature for bullvalene.

We wish to report an nmr investigation of bullvalene in the solid state. A Varian DP-40 spectrometer equipped with a Varian Fieldial magnetic field regulator was used for this study of a powdered sample. Spectra were recorded as the derivative of the absorption curve, and the line widths quoted herein are the separations between maxima and minima in these derivative curves. It may be seen from Figure 1, where the line width is plotted as a function of temperature, that above 0° the line width begins to decrease as the temperature is raised. This reduction in line width can be ascribed to molecular motion which averages the direct dipole-dipole interaction of the hydrogen nuclei. In bullvalene this motion may be reorientation about a molecular axis or possibly valence isomerization which has been observed in solution.<sup>3,4</sup> The observed second moment of 10 gauss<sup>2</sup> for the spectrum at -33° is a reasonable value for a rigid lattice. At a temperature of 83°, which is above the line-width transition, the second moment is reduced to 5 gauss<sup>2</sup>. This is larger than the value which would be expected for general reorientation of the molecules in the crystal lattice.

If it is assumed that the process which narrows the resonance line is an activated one, then it is possible to calculate an activation energy<sup>5</sup> from the line-width data in Figure 1. A value of 9.2 kcal/mole is obtained for the activation energy and  $0.2 \times 10^{12} \text{ sec}^{-1}$  for the frequency factor which may be compared with the solution results of 11.8 kcal/mole and  $0.8 \times 10^{13} \text{ sec}^{-1}$ .<sup>4</sup>

In a further attempt to characterize the motion in solid bullvalene, the nmr spectra of the dimer of cyclo-octatetraene, which melts at 76° and which is the precursor in the photochemical synthesis of bullvalene,<sup>1</sup> were examined. Because of its shape this dimer would not be expected to undergo reorientation in the solid. It is, however, a derivative of homotropylidene and is thus capable of valence isomerization. Line widths for this material were measured from -170° up to the melting point and were found to be essentially constant in this temperature range with a value of approximately 10.5 gauss. This observation does not preclude the possibility of observing the effect of valence isomerization in the solid because in the case of the dimer only

(5) H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, **18**, 162 (1950).

some of the protons would be affected by this process. A better molecule to study in this regard would be homotropylidene.

If the line-width transition shown in Figure 1 is due to reorientation, then it is possible that bullvalene belongs to a special class of solids, the so-called plastic crystals, in which case it should undergo a crystal-crystal transition and the molecules in the high-temperature crystalline form would reorient.

We have also observed that below 0° bullvalene apparently has a long relaxation time since time intervals of several minutes are required before spectra with reproducible intensities can be observed.

**Acknowledgment.** We are indebted to Union Carbide European Research Associates for the materials studied in this work.

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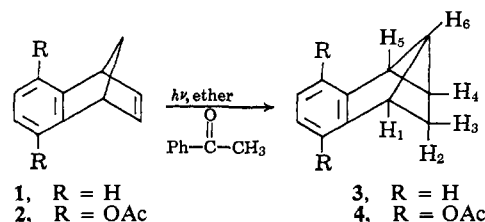
Union Carbide Corporation, Chemicals Division, Research and Development, South Charleston, West Virginia 25303

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## The Photorearrangement of Benzonorbornadienes

Sir:

The photoisomerization of norbornadienes to quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptanes (quadricyclanes) appears quite general.<sup>1</sup> We report at this time the isomerization of benzonorbornadienes when irradiated in the presence of a sensitizer to tetracyclo[5.4.0.0<sup>2,4</sup>.0<sup>3,6</sup>]undecal(7),8,10-trienes.



Irradiation of a 1% solution of benzonorbornadiene<sup>2</sup> (1) in ether containing 0.01% acetophenone for 24 hr with a bank of 16 F8T5·BLB bulbs<sup>3</sup> gave 95% conversion<sup>4</sup> to 3; bp 220° (760);  $n_D^{27} 1.5742$ . *Anal.* Calcd for C<sub>11</sub>H<sub>10</sub>: C, 93.04; H, 6.96; mol wt, 142. Found: C, 92.52; H, 7.12; mol wt, 142 (mass spectroscopy). The structure of compound 3 was established by its nmr spectrum and the isomerization 2 → 4. The nmr spectrum<sup>5</sup> contained a complex aromatic region at  $\delta$  7.45–6.78 with an integrated intensity of 4 compared to the aliphatic region. The aliphatic region

(1) (a) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961); (d) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (e) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 1270 (1964); (f) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964); (g) D. M. Lamal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965); (h) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, **30**, 2259 (1965).

(2) G. Wittig and E. Knauss, *Ber.*, **91**, 895 (1958).

(3) Rayonet photochemical reactor from the Southern N. E. Ultraviolet Co. F8T5·BLB bulbs peak at 3500 Å; G8T5 bulbs have maximum output at 2537 Å.

(4) Based on glpc peak areas.

(5) Compound 3 run in CCl<sub>4</sub>-TMSi, 4 in CDCl<sub>3</sub>-TMSi;  $\delta$  values in parts per million downfield from TMSi at 0.