to those of an authentic sample (b.p. 189–190°, n^{20}D 1.4902).

2-Phenylpentane was isolated in a cut boiling at 192.4–193.3°, n^{20}D 1.4893, the infrared spectrum of which was identical to that of an authentic sample (b.p. 192–192.6°, n^{20}D 1.4882).

2,3-Diphenylbutane crystallized from cuts boiling at 100–110° at 1.5 mm. Recrystallization from aqueous ethanol yielded white crystals, m.p. 126–126.5° (lit.[58] m.p. 126–127°). The infrared spectrum (carbon disulfide solvent) had characteristic bands at 12.93 and 13.22 μ as reported in the literature.[55]

Experiment 15 (Ethylbenzene–Isobutylene).—Isobutylene dimers were found in a cut boiling at 95–114°, n^{20}D 1.4217. Chromatographic removal of arenes followed by distillation yielded the major product, 1,1,3-trimethylcyclopentane, b.p. 104.0–104.2°, n^{20}D 1.4101 (lit.[59] b.p. 104.9°, n^{20}D 1.4112). The infrared spectrum exhibited the characteristic bands of the authentic cyclane (A.P.I. 525).[54]

2-Methyl-4-phenylpentane was identified in a cut boiling at 200–205°, n^{20}D 1.4869, the infrared spectrum of which was essentially identical to that of the synthetic sample IV.

Isohexylbenzene was purified by redistillation of a product cut; it boiled at 216.2–216.9°, n^{20}D 1.4867. Its infrared spectrum was identical to that of the synthetic sample VII.

Experiments 16—18 (Cumene–Propylene).—Due to the low yields of monoadduct products, the cuts were combined (a small sample of each was saved for subsequent infrared analysis) into two charges for redistillation: b.p. 196–209°, 5.23 g.; b.p. 206–213°, 7.40 g. After 12 chromatographs of the resultant cuts, spectral identification was possible.

2-Methyl-2-phenylpentane was identified in cuts boiling at 207–211°. Chromatography yielded a cut having n^{20}D 1.4901, which had an infrared spectrum practically identical to that of an authentic sample (b.p. 207–208°, n^{20}D 1.4936), except for the presence of weak bands due to the possible presence of 2-methyl-1-phenylpentane.

2-Methyl-1-phenylpentane was indicated in product cuts, but its presence could not be positively established due to contamination by compounds of higher refractive index which were not readily separable by chromatography. A

cut boiling at 213–226°, n^{20}D 1.4967, had an infrared spectrum which strongly resembled that of an authentic sample (b.p. 218°, n^{20}D 1.4875; synthesized by Mr. C. T. Chen) except for foreign bands at 13.14 and 13.38 μ, which may have been caused by higher boiling contaminants.

1,1,3-Trimethylindan was found in a cut boiling at 204.6–205.0°; chromatography yielded a purified fraction with n^{20}D 1.5047. Except for the presence of a band in the 14.3 μ region due to minor amounts of hexylbenzene contaminants, the infrared spectrum was identical to that of the synthetic sample VIII.

1,1,2-Trimethylindan was detected in a cut boiling at 209–211°; chromatography afforded a purified fraction having n^{20}D 1.5097. The infrared spectrum was identical to that of an authentic sample[53] (b.p. 211° cor. to 760 mm., n^{20}D 1.5120) except for a 14.3 μ band due to the presence of a small amount of hexylbenzene impurities.

Experiment 19 (Cumene–Isobutylene).—The extremely low monoadduct yield precluded redistillation of these cuts; however, chromatography allowed the identification of two components, and the presence of certain expected compounds in the unidentified portion was excluded.

1,1,3,3-Tetramethylindan was found in a cut boiling at 187–210°; an enriched chromatographic fraction had n^{20}D 1.4950. Aside from extraneous bands due to alkylbenzene contaminants, the infrared spectrum demonstrated the presence of the compound. Especially evident were the 7.54–7.60 μ doublet and the 13.18 μ main band, identical to those of the synthetic sample IX.

2,4-Dimethyl-1-phenylpentane was isolated in a cut boiling at 224.2–225.7°, which had n^{20}D 1.4831 after chromatography. Except for a minor foreign band at 13.10 μ, its infrared spectrum was identical to that of a synthetic sample V.

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(58) E. Ellingboe and R. C. Fuson, THIS JOURNAL, **55**, 2960 (1933).

(59) Selected Values of Properties of Hydrocarbons, American Petroleum Institute Research Project 44, Table 15a, October 31, 1952.

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

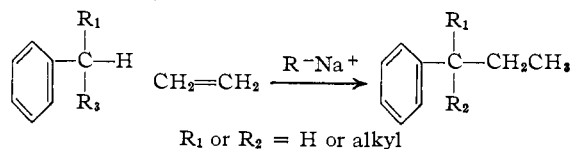# The Potassium-catalyzed Reaction of Olefins with Arylalkanes[1]

BY LUKE SCHAAP[2a] AND HERMAN PINES[2b]

The reaction of ethylene with toluene, ethylbenzene, cumene and cyclohexylbenzene catalyzed by potassium and anthracene was studied. Besides the "normal" side chain ethylation the reaction was accompanied by a cyclization resulting in the formation of indans. The reaction of propylene with cumene resulted in the formation of 2,3-dimethyl-2-phenylbutane, 1,1,2- and 1,1,3-trimethylindan. The presence of the last compound indicates for the first time the formation of a secondary alkylcarbanion as an intermediate in the alkylation reaction. The ethylation of the aromatic nucleus of t-butylbenzene catalyzed by potassium takes place under the same condition as the side chain ethylation of compounds having benzylic hydrogens. The mechanism of alkylation and cyclization is discussed.

The sodium-catalyzed ethylation of arylalkanes has been shown to produce compounds in which the benzylic hydrogens of the arylalkanes are replaced by ethyl groups.[3]

R_1 or R_2 = H or alkyl

This method has proved to be useful for the synthesis of such hydrocarbons in a pure state. A carbanion mechanism has been proposed for this reaction.[3]

Benzene and arylalkanes having no benzylic hydrogens react with ethylene only under more vigorous conditions to yield products in which the aromatic ring has been ethylated.[4]

The mode of addition of arylalkanes to substituted ethylenes has been shown to be highly selective. The compounds produced are those that

(1) Paper X of the series of Base-catalyzed Reactions. For paper IX see H. Pines and L. Schaap, THIS JOURNAL, **79**, 2956 (1957).

(2) (a) Predoctoral fellow: Universal Oil Products Co. 1954–1955, Standard Oil Co. (Indiana) 1955–1956. (b) To whom requests for reprints should be addressed.

(3) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955).

(4) H. Pines and V. Mark, ibid., **78**, 4316 (1956).

TABLE I

POTASSIUM-CATALYZED ALKYLATION REACTIONS OF ⟨phenyl⟩–R

Expt.	R =	Olefin[a]	Conditions °C.	Hr.	Yield of monoadduct[b] mole %	Products[c] Compounds	Distribution mole %
1	CH₃	C₂H₄	190 ± 5	11	53	n-Propylbenzene	98
						Indan	2
2	C₂H₅	C₂H₄	190 ± 2	3	64	sec-Butylbenzene	86
						1-Methylindan	14
3	i-C₃H₇	C₂H₄	192 ± 4	7	34	t-Pentylbenzene	51
						1,1-Dimethylindan	49
4	i-C₃H₇	C₂H₄	245 ± 3	2.5	22	t-Pentylbenzene	49
						1,1-Dimethylindan	51
5	i-C₃H₇[d]	C₂H₄	185 ± 1	3.5	33	t-Pentylbenzene	66
						1,1-Dimethylindan	34
6	i-C₃H₇	C₂H₄[e]	190 ± 4	3	39	t-Pentylbenzene	75
						1,1-Dimethylindan	25[f]
7	cyclo-C₆H₁₁[g]	C₂H₄	186 ± 4	5	13[h]	1-Ethyl-1-phenylcyclohexane	63
						Spiro-(cyclohexane-1,1'-indan)[i]	37
8	t-C₄H₉	C₂H₄	190 ± 2	11	18	sec-Butyl-x-t-butylbenzenes	
9	i-C₃H₇[k]	C₃H₆	208–233	6.5	4.4	2,3-Dimethyl-2-phenylbutane	52
						1,1,2-Trimethylindan	27
						1,1,3-Trimethylindan	21

[a] One mole of aromatic hydrocarbon was used in each reaction with 0.2 mole of the olefin and a catalyst consisting of 1.7 g. (0.0435 g. atom) of potassium with 1 g. of anthracene. [b] Yields are based on the amount of olefin charged. [c] Recovered gases usually consisted of approximately 20–30% of the recovered olefin and 70–80% of the corresponding saturated hydrocarbon. Little hydrogen was obtained. The yield of hydrogenated olefin produced was greater than that of the indan on a molar basis. [d] Sodium, 3.4 g. (0.148 g. atom), was added to the potassium catalyst used in this reaction. [e] A higher conversion of isopropylbenzene to ethylated product was obtained by using 0.5 mole of ethylene in this reaction. [f] 1,1-Dimethyl-3-ethylindan, 3.33 g. (0.019 mole), also was obtained. [g] Half the usual amount of the aromatic hydrocarbon and olefin was used in this reaction. [h] Biphenyl, 0.5%, based on phenylcyclohexane charged also was obtained. [i] The presence of this compound is inferred as indicated in the Experimental part. [k] Potassium, 4 g. (0.1 g. atom), was used. A similar reaction (experiment 10) was carried out at 245° using no potassium, and no adducts were formed.

would be expected from the addition of the intermediate benzylic carbanion to the olefin in such a manner as to produce a primary carbanion rather than a less stable secondary or tertiary carbanion.[4]

The present investigation shows that additional products to those cited above are obtained when potassium is used instead of sodium in carrying out reactions of arylalkanes with ethylene. An internal alkylation may take place forming indans.

R₁ or R₂ = H or alkyl
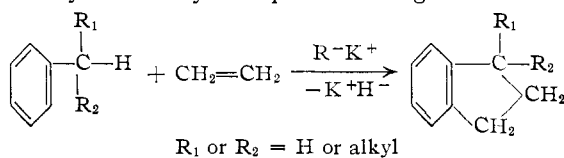
The apparatus and experimental conditions used in the present study were similar to those used for sodium-catalyzed reactions.[3,4] The results obtained are summarized in Table I. The ratio of indan to monoalkylbenzene produced depends on the extent of substitution of the α-carbon of the arylalkane; it increases on going from toluene to ethylbenzene to isopropylbenzene. An increase of temperature from 190 to 245° has little effect on this ratio. The presence of sodium in the potassium catalyst causes an increase in the amount of "normal" product indicating that both metals can take part in the ethylation reaction. If the molar ratio of ethylene to isopropylbenzene charged is increased from 0.2 to 0.5, the ratio of t-pentylbenzene to 1,1-dimethylindan in the reaction product is also increased. This increase is due to the fact that the indan produced reacts

with ethylene to form 1,1-dimethyl-3-ethylindan, while t-pentylbenzene having no benzylic hydrogen does not react.

Phenylcyclohexane also reacts with ethylene to form 1-ethyl-1-phenylcyclohexane and spiro-(cyclohexane-1,1-indan) and a small amount of biphenyl. The dehydrogenation of phenylcyclohexane to biphenyl using a sodium catalyst has been previously reported to occur at higher temperatures.[5]

Nuclear alkylation takes place when t-butylbenzene is treated with ethylene at 190° using a potassium catalyst. Inasmuch as the ethyl-x-t-butylbenzenes are more reactive than t-butylbenzene, products resulting from the reaction of t-butylbenzene with two molecules of ethylene were obtained. Cyclization may accompany the addition of the second molecule of ethylene, but the products were probably largely sec-butyl-x-t-butylbenzenes. A similar reaction of t-butylbenzene and ethylene catalyzed by sodium occurs but at much higher temperatures.[5]

The reaction of isopropylbenzene with propylene catalyzed by potassium produced not only 2,3-dimethyl-2-phenylbutane and 1,1,2-trimethylindan but also 1,1,3-trimethylindan indicating that the cyclization reaction does not show the selectivity that the simple alkylation reaction does. None of these products can be attributed to a similar thermal reaction which takes place only at a much higher temperature.[6]

(5) H. Pines and M. Kolobielski, This Journal, 79, 1698 (1957).
(6) H. Pines and J. T. Arrigo, ibid., 79, 4958 (1957).

Discussion and Mechanism

The mechanism of the reaction between aryl-alkanes and olefins in the presence of potassium is similar to that which has been suggested previously for sodium.[3,7] However the adduct of the benzylic carbanion with ethylene is a very reactive alkyl carbanion, and cyclization can take place by the attack of this carbanion on the aromatic ring followed by elimination of a hydride ion.[8]
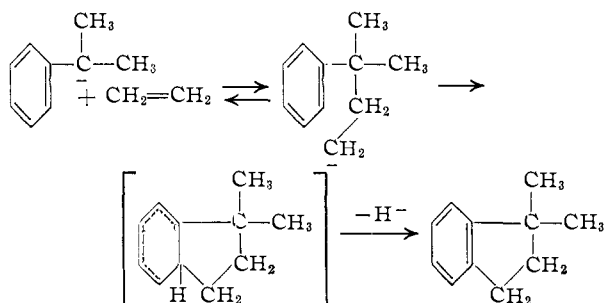
The reaction of alkylpotassium compounds with benzenes at temperatures above 60° has been reported by Bryce-Smith and Turner.[9]

The increase in the rate of indan formation vs. the "normal product" with increasing substitution on the α-carbon of the arylalkane can be interpreted as being due to: (a) a decrease in the rate of the chain propagation steps (abstraction of a benzylic hydrogen by the carbanion formed on addition to the olefin) in going from compounds with more acidic (primary) hydrogens to compounds with less acidic (secondary or tertiary) hydrogens and to (b) the steric effect of the methyl groups on the α-carbon which tend to hold the carbanion produced in close proximity to the aromatic ring facilitating the cyclization reaction. The "geminal effect" of substituents on rates of ring closures is well known.[10] Since the chain propagation step was shown[7] to be a very fast step in the side chain ethylation reaction, the steric effect as indicated under (b) must be the controlling factor in the cyclization reaction to form indans. It has been shown by Brown and van Gulick[11] that this effect is at a maximum when the substitution is at the carbon in the middle of the chain which closes to form a 5-membered ring. A similar enhancement of cyclization was observed in thermal reactions of isopropylbenzene with olefins.[6]

The nuclear ethylation of t-butylbenzene may take place by means of two possible chain carbanion mechanisms as was suggested previously for the reaction of isobutylbenzene with ethylene.[4] The formation of ethylpotassium by the addition of potassium hydride to ethylene and the facile attack

of this carbanion on the aromatic nucleus probably explains why this reaction takes place under relatively mild conditions when catalyzed by potassium.

The presence of 1,1,3-trimethylindan in the reaction product of propylene with isopropylbenzene indicates for the first time that a benzylic carbanion can add to an olefin to form a secondary carbanion. Such an adduct should be very unstable and should undergo the reversal of the addition reaction rather than the intermolecular chain propagation reaction which would result in the formation of 2-methyl-2-phenylpentane. The adduct, being very reactive, can undergo the intramolecular cyclization reaction to form 1,1,3-trimethylindan. An alternative explanation of the formation of this indan is that the addition of the benzylic carbanion to the olefin and the ring closure are concerted reactions so that carbanion stability does not influence the formation of cyclized products.

Experimental

General Procedure.—The reactions were carried out using a 250-ml. Magne-Dash[12] autoclave. Weighed amounts of the arylalkane and catalyst were placed in this, and air was flushed from the closed autoclave with the hydrocarbon gas used in the experiment. Measured amounts of this gas were then added, and the autoclave was heated to the desired temperature. The reaction was allowed to proceed until no more pressure drop was observed, and after cooling to 60° gases were vented and measured. Samples of the gases were analyzed by mass spectrometer. The liquid product was filtered and the catalyst residue was decomposed using t-butyl alcohol. Most of the unreacted hydrocarbon was removed by distillation and the alkylated product was fractionated using a Piros–Glover column. The infrared spectra of these fractions were taken next using a 0.041-mm. cell and a Baird double beam recording spectrophotometer. The product distribution was calculated by comparing with the spectra of authentic samples or known mixtures of the compounds present. Table II lists the analytical bands used.

TABLE II
ANALYTICAL INFRARED BANDS

Compound	Wave length, μ
Indan	10.72
3-Phenylpentane	9.47
sec-Butylbenzene	11.02
1-Methylindan	10.70
t-Pentylbenzene	12.73
1,1-Dimethylindan	13.72
Phenylcyclohexane	11.28
1-Ethyl-1-phenylcyclohexane	7.24
Spiro-[cyclohexane-1,1'-indan]	13.75
2,3-Dimethyl-2-phenylbutane	12.62
1,1,2-Trimethylindan	8.21
1,1,3-Trimethylindan	8.51

Experiment 1.—Practically all of the product consisted of n-propylbenzene, b.p. 156–160°, n^{20}D 1.4918. Intermediate fractions boiling between propylbenzene and diethylated material (1.78 g. of 3-phenylpentane was obtained) showed the presence of indan.

Experiment 2.—The sec-butylbenzene, b.p. 172–174°, n^{20}D 1.4898, was largely separated from the 1-methylindan by distillation. By means of redistillation of the higher boiling fractions followed by chromatography over silica gel, 1-methylindan of higher than 95% purity was obtained, b.p. 186°, nD^{20} 1.5240.

Experiment 6.—Diethylated material, b.p. 113.3–114.9° at 22 mm. (cor. 227°), n^{20}D 1.5049–1.5060, was obtained. This material had an infrared spectrum which closely re-

(7) H. Hart, THIS JOURNAL, **78**, 2619 (1956).

(8) The reaction of such a carbanion to form an indan has been demonstrated by allowing 3 methyl-3-phenyl-1-chlorobutane and potassium to react at 80°. 1,1-Dimethylindan, 6.4%, and t-pentylbenzene, 4.8%, were produced in addition to carbanion elimination products (unpublished work, H. Pines and L. Schaap).

(9) D. Bryce-Smith and E. E. Turner, J. Chem. Soc., 861 (1953).

(10) A discussion of this effect by G. S. Hammond may be found in "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 462–470.

(11) R. F. Brown and N. M. van Gulick, J. Org. Chem., **21**, 1046 (1956).

(12) Autoclave Engineers, Inc., Erie, Penna.

sembled that of 1,1,3-trimethylindan having a strong split band at 13.15 and 13.43 μ. This is 1,1-dimethyl-3-ethyl-indan which also contained a small amount of m-t-pentyl-ethylbenzene as was indicated by weak infrared bands at 12.55 and 14.12 μ.

Anal. Calcd. for $C_{12}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.40; H, 10.46.

Material boiling in the range of 120–144° at 22 mm., 3.5 g., was also obtained which had infrared spectra characteristic of indans.

Experiment 7.—Spiro[cyclohexane-1,1'-indan] was neither isolated in a pure state from this reaction nor was it synthesized, but it was assumed to be present because of the strong infrared band at 13.75 μ found in the higher boiling (b.p. 132–137° at 10 mm.) fractions of the product. Absorption in the 13.7–13.8 μ region is usually characteristic of 1,1-disubstituted indans. The amount of this compound was determined by difference. Spiro-(cyclohexane-1,1'-indan), b.p. 132–133° at 10 mm., has been prepared by Levitz, Perlman and Bogert.[13]

Biphenyl was shown to be present by the 13.52 μ infrared band, and the amount present was estimated using the 246 mμ band of the ultraviolet spectrum in 95% ethanol.

Experiment 8.—Only diethylated material, b.p. 105–125° at 15 mm., was obtained. The product had strong infrared absorption bands at 12.65 and 14.12 μ showing m-disubstitution, a strong band at 12.05 μ indicating p-disubstitution and a weaker band at 13.21 μ suggesting o-disubstitution.

Experiment 9.—The monoalkylated fractions were collected at 81–85° at 10 mm. Higher boiling material (2.6 g.), b.p. 170–185° at 9 mm., n^{20}D 1.5516–1.5600, also was obtained. The infrared spectra of this showed medium intensity bands at 11.25, 11.92 and 13.12 μ and strong bands at 12.63 and 14.18 μ. The boiling point, refractive index and infrared spectra indicate that this is a mixture of diisopropylbiphenyls; probably largely 3,3'-diisopropylbiphenyl. The formation of biphenyls has been observed previously with sodium catalysts.[4]

Synthesis of 1-Methylindan.—1-Methyl-1-indanol was prepared by the reaction of methylmagnesium iodide on 1-indanone. The product of this reaction was obtained in a 59% yield and crystallized on distillation, b.p. 102–104° at

(13) M. Levitz, D. Perlman and M. T. Bogert, *J. Org. Chem.*, **6**, 105 (1941).

6 mm., m.p. 56–57° recrystallized from ligroin; literature[14] b.p. 118° at 14 mm.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.48; H, 8.19.

This alcohol was treated with hydrogen under pressure at 220° using a copper–chromite catalyst to yield 1-methyl-indan, b.p. 190° at 748 mm., n^{20}D 1.5253; literature[15] b.p. 189.5° at 739.2 mm., n^{25}D 1.5241. The infrared spectrum of the compound obtained is identical with that reported.[15]

Synthesis of 1,1-Dimethylindan.—3,3-Dimethyl-1-indanone,[16] b.p. 128° at 19 mm., was treated with hydrogen under pressure at 220° using a copper–chromite catalyst. A 22% yield of hydrocarbon, b.p. 82.5–85° at 21 mm., n^{20}D 1.5187, was obtained which contained some of the corresponding indene. Therefore, this was selectively hydrogenated using a 10% palladium-on-charcoal catalyst to yield 1,1-dimethyl-indan, n^{20}D 1.5141; literature[17] b.p. 191°.

Synthesis of 1,1,2-Trimethylindan.—This hydrocarbon was prepared using the method of Bogert and Davidson.[17] 2,3-Dimethyl-1-phenyl-2-butanol, b.p. 125° at 17 mm., n^{20}D 1.5115, was treated with 85% sulfuric acid. An 88% yield of hydrocarbon was obtained, but some of the unsaturated uncyclized product remained which was removed by treating it with toluene in 96% sulfuric acid to yield the pure 1,1,2-trimethylindan, b.p. 86° at 10 mm. (cor. 211°), n^{20}D 1.5120; literature[18] b.p. 208°, n^{25}D 1.5101.

1,1,3-Trimethylindan.—The synthesis of this hydrocarbon, b.p. 203.9–204.8° at 748 mm., n^{20}D 1.5082, has been reported previously.[6]

Acknowledgment.—The authors wish to express their appreciation to Professor D. F. Mason of the Chemical Engineering Department for the mass spectral analysis and to Miss H. Beck for the elementary analysis.

(14) J. von Braun and G. Kirschbaum, *Ber.*, **46**, 3041 (1913).
(15) J. Entil, C. E. Ruof and H. C. Howard, *Anal. Chem.*, **25**, 1303 (1953).
(16) This compound was kindly provided by H. L. Dryden, Jr.
(17) M. T. Bogert and D. Davidson, THIS JOURNAL, **56**, 185 (1934).
(18) D. Price, D. Davidson and M. T. Bogert, *J. Org. Chem.*, **2**, 540 (1938).

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The Benzoylation of Cyclopentadienyllithium

BY WILLIAM J. LINN AND WILLIAM H. SHARKEY

Cyclopentadienyllithium has been shown to react with aromatic acid chlorides to give products in which the cyclopentadiene ring is substituted with two aroyl groups in the 1- and 5-positions. These diaroyl derivatives are considered as substituted fulvenes because they exist mostly in the enolic form.

A number of reactions of the cyclopentadienyl anion have appeared in the literature, but there has been no report of the treatment of metallic derivatives of cyclopentadiene with acid halides. For such a study we chose to use cyclopentadienyllithium which is easily prepared from cyclopentadiene and phenyllithium.[1]

Aromatic acid chlorides reacted with cyclopentadienyllithium to form 1-aroyl-6-hydroxy-6-aryl fulvenes in yields of 25–50%. The identity of the products and a suggested mechanism for their formation were inferred from a study of the reaction of cyclopentadienyllithium with benzoyl chloride.

The reaction of an ethereal suspension of cyclo-

(1) W. von E. Doering and C. H. DePuy, THIS JOURNAL, **75**, 5955 (1953).

pentadienyllithium with benzoyl chloride gave an orange crystalline solid. Elemental analysis and molecular weight determination indicated that this material was a dibenzoyl derivative of cyclopentadiene. Other chemical and physical evidence has shown that the reaction product is an enol, 1-benzoyl-6-hydroxy-6-phenylfulvene (I).
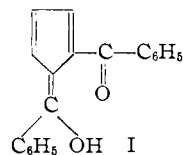
Evidence for this enol was furnished by determination of the proton magnetic resonance spec-