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-ethylindan which also contained a small amount of *m-t*-pentylethylbenzene 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., $n^{20}\text{D}$ 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 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-methylindan, b.p. 190° at 748 mm., $n^{20}\text{D}$ 1.5253; literature[15] b.p. 189.5° at 739.2 mm., $n^{25}\text{D}$ 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., $n^{20}\text{D}$ 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-dimethylindan, $n^{20}\text{D}$ 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., $n^{20}\text{D}$ 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°), $n^{20}\text{D}$ 1.5120; literature[18] b.p. 208°, $n^{25}\text{D}$ 1.5101.

1,1,3-Trimethylindan.—The synthesis of this hydrocarbon, b.p. 203.9–204.8° at 748 mm., $n^{20}\text{D}$ 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.

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

[14] J. von Braun and G. Kirschbaum, *Ber.*, **46**, 3041 (1913).

[15] J. Entil, C. K. 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).

EVANSTON, ILLINOIS

[CONTRIBUTION NO. 386 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO.]

The Benzoylation of Cyclopentadienyllithium

BY WILLIAM J. LINN AND WILLIAM H. SHARKEY

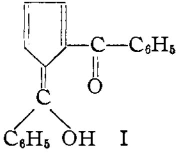
RECEIVED APRIL 16, 1957

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 cyclopentadienyllithium 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).



I

Evidence for this enol was furnished by determination of the proton magnetic resonance spec-

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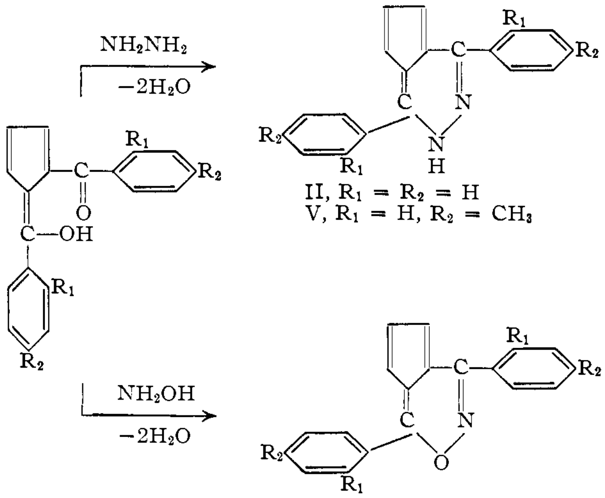
[1] W. von E. Doering and C. H. DePuy, THIS JOURNAL, **75**, 5955 (1953).

trum.[2] Proton resonance appeared at 240 c.p.s. relative to the proton magnetic resonance absorption of water at a frequency of 30 Mc., which is indicative of a molecule containing a chelated proton. This may be explained by the existence of a hydrogen bond between the enol and the carbonyl of the 1-benzoyl group. Comparison of the area under the 240 c.p.s. band with that of the phenyl proton resonance band indicated that the enol form was present to the extent of at least 90%. The acidity expected of such an enol was demonstrated by its ready solubility in aqueous sodium hydroxide.

The infrared spectrum of the reaction product did not show absorption below 6.1 μ in the region normally assigned to carbonyl groups. However, this is consistent with the hydrogen-bonded enol structure, since it has been shown that conjugation and chelation lead to a large shift of the carbonyl infrared band.[3]

The presence of carbonyl was demonstrated by the formation of crystalline derivatives with hydroxylamine and with hydrazine. In each case the fulvene compound reacted with only *one* mole of the carbonyl reagent with the elimination of *two* moles of water. The hydrazine and hydroxylamine derivatives can be formulated logically as the bicyclic pyridazine I and oxazine II, respectively.



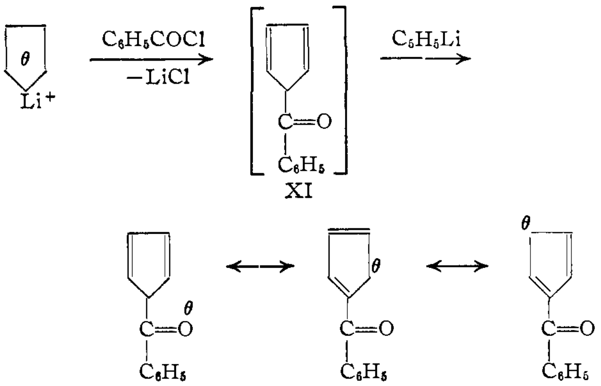
II, $R_1 = R_2 = H$
V, $R_1 = H$, $R_2 = CH_3$

I, $R_1 = R_2 = H$
IV, $R_1 = H$, $R_2 = CH_3$
VII, $R_1 = H$, $R_2 = Cl$
IX, $R_1 = Cl$, $R_2 = H$
X, $R_1 = H$, $R_2 = NO_2$

III, $R_1 = R_2 = H$
VI, $R_1 = H$, $R_2 = CH_3$
VIII, $R_1 = H$, $R_2 = Cl$

Hale has reported that 2,3-dibenzoyl-5-nitrocyclopentadiene forms only an unstable monohydrazone which, when heated with alkali, rearranges and loses water to give a bicyclic pyridazine.[4] However, the possibility that our reaction product might be an isomeric dibenzoylcyclopentadiene, which rearranges on formation of the carbonyl derivatives, is precluded by the spectral evidence.

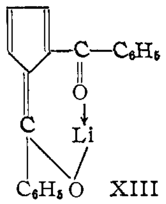
The following explanation is offered as a possible mechanism of formation of the disubstituted cyclopentadiene. Reaction of one mole of cyclopentadienyllithium may produce the intermediate monoketone XI. The remaining hydrogen on the allylic carbon should be removed easily by a second mole of cyclopentadienyllithium to form the resonance stabilized anion XII. It is visualized that the last step is attack by a second mole of benzoyl chloride.



XI

XII

Higher substituted derivatives might be expected on the basis of this mechanism. In no case could more than a single crystalline product be isolated. It is possible that the dibenzoyl derivative isolated may be stabilized by the formation of a lithium salt of the type represented by XIII.



XIII

The highest yield of I that could be isolated was 37%. In every case small amounts of tarry material also were produced. Various modifications of the reaction procedure including change of solvent, low temperatures and inverse addition of the reagents were tried in unsuccessful attempts to increase the yield.

The benzoylation of cyclopentadienyllithium has also been extended to substituted benzoyl chlorides. Yields of 1,5-diaroylcyclopentadienes ranging from 26–50% have been obtained from *p*-toluyl, *o*- and *p*-chlorobenzoyl and *p*-nitrobenzoyl chlorides. The *p*-toluyl and *p*-chlorobenzoyl derivatives were converted to the corresponding oxazines to demonstrate their relationship to the parent compound. Stable crystalline sodium and potassium salts were prepared from the fulvene obtained from *p*-chlorobenzoyl chloride. When these salts were acidified, the original fulvene was regenerated as shown by mixed melting point determinations.

Experimental

1-Benzoyl-6-hydroxy-6-phenylfulvene (I).—Phenyllithium was prepared in the usual manner from 15.7 g. (0.1 mole) of bromobenzene and 1.4 g. (0.2 mole) of lithium shavings in

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[2] We are indebted to Dr. W. D. Phillips of these laboratories for the determination and interpretation of the proton magnetic resonance.

[3] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[4] W. J. Hale and L. Thorp, *ibid.*, **35**, 68 (1913); W. J. Hale, *ibid.*, **38**, 2535 (1916).

150 ml. of ether. To this solution, 6.6 g. (0.1 mole) of freshly distilled cyclopentadiene was added dropwise. The suspension of white cyclopentadienyllithium was stirred for 15 minutes, and 14.1 g. (0.1 mole) of benzoyl chloride was added dropwise. There was an immediate formation of a bright yellow color. Stirring was continued for 0.5 hr. after the addition was complete, and the reaction mixture was hydrolyzed with dilute aqueous acetic acid. The ether layer was separated and the aqueous layer extracted twice more with ether. After the combined extracts had been dried over Drierite, the solvent was removed by evaporation to leave a brick-red solid. After recrystallization from glacial acetic acid, which removed combined lithium salts, there was obtained 5.1 g. (37%) of orange crystals of the fulvene, m.p. 101–102°. The melting point was raised to 102–103° by recrystallization from hexane; $\lambda_{\max}^{\mathrm{EtOH}}$ 264 mμ (log ϵ 4.16), 282 mμ (shoulder) (log ϵ 4.11), 343 mμ (log ϵ 4.01). *Anal.* Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.15; mol. wt., 274.3. Found: C, 83.5, 83.2; H, 5.3, 5.3; mol. wt., 290.

1,4-Diphenylcyclopent[d]-1,2-oxazine (III).—A solution of 1.0 g. of 1-benzoyl-6-hydroxy-6-phenylfulvene and 1.0 g. of hydroxylamine hydrochloride in 5 ml. of absolute ethanol and 5 ml. of pyridine was refluxed for 2 hr. The solvent was removed by evaporation, and the residual solid was washed with water and recrystallized from absolute ethanol to give 0.73 g. (74%) of orange plates of the oxazine, m.p. 143–143.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ 230 mμ (log ϵ 4.29), 244 mμ (log ϵ 4.32), 338 mμ (log ϵ 3.94). *Anal.* Calcd. for $C_{19}H_{13}NO$: C, 84.1; H, 4.8; N, 5.2. Found: C, 84.1; H, 4.9; N, 4.7, 4.8.

1,4-Diphenyl-2-cyclopenta[d]pyridazine (II).—A solution of 1.0 g. of 1-benzoyl-6-hydroxy-6-phenylfulvene and 1.0 g. of 85% hydrazine hydrate in 20 ml. of absolute ethanol was heated under reflux for 2 hr. When the solution was cooled, crystals of the pyridazine separated. There was obtained 0.8 g. (81%) of fluffy yellow crystals, m.p. 205–207°. Recrystallization from absolute ethanol raised the m.p. to 211–212°. *Anal.* Calcd. for $C_{19}H_{14}N_2$: C, 84.4; H, 5.2; N, 10.4. Found: C, 84.6; H, 5.3; N, 10.3, 10.4. The infrared spectrum of the pyridazine exhibited an N–H stretching vibration at 2.97 μ.

Substituted dibenzoylcyclopentadienes were prepared from cyclopentadienyllithium and substituted benzoyl chlorides using procedures similar to that described above.

1-*p*-Toluyl-6-hydroxy-6-*p*-tolylfulvene (IV) was obtained in 44% yield as orange crystals, m.p. 148–149° (from benzene); $\lambda_{\max}^{\mathrm{EtOH}}$ 275 mμ (log ϵ 4.23), 348 mμ (log ϵ 4.04). *Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 83.4; H, 6.0. Found: C, 83.6; H, 6.1.

The corresponding oxazine derivative VI melted at 163–165° dec. (from benzene); $\lambda_{\max}^{\mathrm{EtOH}}$ 233 mμ (log ϵ 4.26), 341 mμ (log ϵ 4.05). *Anal.* Calcd. for $C_{21}H_{17}NO$: C, 84.2; H, 5.7; N, 4.7. Found: C, 84.5; H, 5.8; N, 4.2.

1-*p*-Chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene (VII) was obtained in 50% yield, m.p. 175–177° (from a benzene–hexane mixture). *Anal.* Calcd. for $C_{19}H_{12}O_2Cl_2$: C, 66.5; H, 3.5; Cl, 20.7. Found: C, 66.6; H, 3.7; Cl, 20.5.

The oxazine derivative VIII was formed in 62% yield. It melted at 187–188° dec. (from benzene). *Anal.* Calcd. for $C_{19}H_{11}NOCl_2$: C, 67.1; H, 3.3; N, 4.1; Cl, 20.8. Found: C, 67.5; H, 3.3; N, 4.0; Cl, 20.5.

1-*o*-Chlorobenzoyl-6-hydroxy-6-*o*-chlorophenylfulvene (IX) was formed in 26% yield. The yellow crystals were recrystallized from a mixture of ethyl alcohol and ethyl acetate. The melting point showed considerable variation after each recrystallization. The highest observed was 146–147.5°. *Anal.* Calcd. for $C_{19}H_{12}Cl_2O_2$: C, 66.5; H, 3.55; Cl, 20.6. Found: C, 66.7; H, 3.6; Cl, 20.6.

1-*p*-Nitrobenzoyl-6-hydroxy-6-*p*-nitrophenylfulvene (X) was obtained in 39% yield. Recrystallization from dimethylformamide gave yellow, feathery needles, m.p. 248–250°. *Anal.* Calcd. for $C_{19}H_{12}N_2O_6$: C, 62.6; H, 3.3. Found: C, 63.1; H, 3.6. The fulvene also could be recrystallized from dioxane to give brick-red crystals, m.p. 253–255°. *Anal.* Calcd. for $C_{19}H_{12}N_2O_6$: C, 62.6; H, 3.3. Found: C, 62.7; H, 3.5.

Potassium and Sodium Salts of 1-*p*-Chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene.—A solution of 5 g. of 1-*p*-chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene in 25 ml. of 20% ethanolic potassium hydroxide was refluxed on the steam-bath for 1 hr. The reaction mixture was cooled and the bright yellow solid separated by filtration. After the yellow crystals had been washed twice with cold ethanol and air-dried, the yellow crystals weighed 5.7 g. The salt was recrystallized twice from benzene–ethyl acetate to give yellow needles that decomposed but did not melt in the range 200–215°. *Anal.* Calcd. for $C_{19}H_{11}O_2K$: C, 59.8; H, 2.9; K, 10.3. Found: C, 59.6; H, 3.3; K, 9.9.

A sample of the potassium salt was dissolved in boiling glacial acetic acid. The crystals which deposited when the solution cooled were collected by filtration and washed with water. The yellow crystals melted at 173–174° after one recrystallization from hexene containing a little benzene. The melting point of a mixture of this material and 1-*p*-chlorobenzoyl-6-hydroxy-6-*p*-chlorophenylfulvene (m.p. 174–176°) was 174–176°.

The sodium salt was prepared in a similar manner except that sodium ethoxide was prepared by dissolving sodium in ethanol. From 1.0 g. of the fulvene there was obtained 0.5 g. of yellow crystals that did not melt or decompose below 250°. Analysis indicated that this salt crystallized with 2 molecules of water. *Anal.* Calcd. for $C_{19}H_{11}O_2Cl_2Na\cdot 2H_2O$: C, 56.9; H, 3.8; Na, 5.7. Found: C, 57.3; H, 3.6; Na, 5.9.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Thermal Condensation of Formaldehyde with Acyclic Olefins[1]

BY A. T. BLOMQUIST, M. PASSER,[2] C. S. SCHOLLENBERGER[2] AND JOSEPH WOLINSKY[2]

RECEIVED MARCH 30, 1957

Thermal condensation of formaldehyde with 1- and 2-heptene, 2-methyl-1-heptene and 2-ethyl-1-butene in solvent acetic acid affords, respectively, the acetates of *trans*-3-octen-1-ol, a mixture of 2-methyl-3-hepten-1-ol (70%) and 2-vinyl-1-hexanol (30%), 3-methylene-1-octanol and 3-ethyl-3-penten-1-ol. These observations are in agreement with the postulation that reaction proceeds *via* a planar six-membered ring transition state.

The behavior of a representative group of acyclic olefins in the thermal condensation with formaldehyde has been studied with the object of establishing the scope and limitations of the reaction as a useful synthetic method for unsaturated primary alcohols and related compounds. Another objective was to obtain additional knowledge pertinent to the operating mechanism.

Various workers have shown that the principal

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[1] The work reported here was done as part of a general research program in organic chemistry at Cornell University sponsored by The B. F. Goodrich Co.

[2] Abstracted from part of the dissertations presented by M. Passer in September, 1948, C. S. Schollenberger in September, 1947, and J. Wolinsky in June, 1956, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.