[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

THE REACTION OF AZIBENZIL WITH OLEFINS[1]

C. S. MARVEL AND MELVIN I. KOHAN

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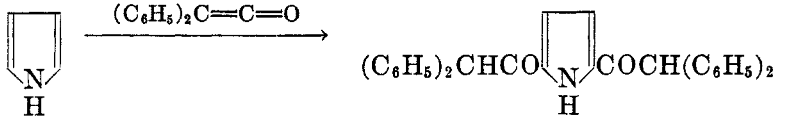
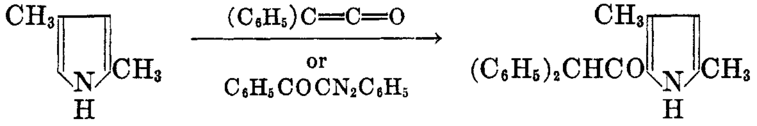
It has been reported previously that phenylbenzoyldiazomethane (azibenzil) undergoes reaction with pyrrole to form 2,5-bis(diphenylacetyl)pyrrole (I) and with 2,4-dimethylpyrrole to form 2,4-dimethyl-5-diphenylacetylpyrrole (II) (1).

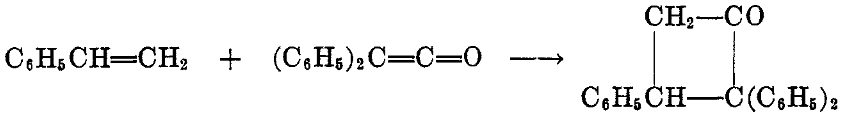


I

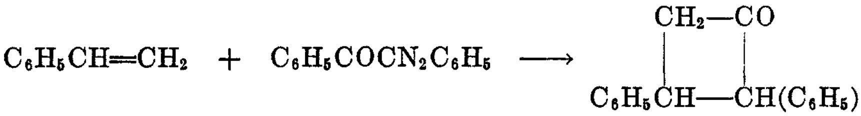


II

Presumably decomposition of the azibenzil produced diphenylketene which was the actual reagent, and it was demonstrated that the reaction of diphenylketene with 2,4-dimethylpyrrole yielded the same product. Since a study of the reaction of diphenylketene with olefins has been in progress in this laboratory, an examination of the action of azibenzil on olefins was undertaken in the hope of eliminating the necessity of isolating the sensitive ketene.



III



III

and/or $(C_6H_5)_2CHCOCH{=}CHC_6H_5 + N_2$

IV

Because of its availability and reactivity towards diphenylketene, styrene was the olefin first studied. When an acetone or a diethyl ether solution of the reagents was heated under reflux for several hours, the expected 2,2,3-triphenylcyclobutanone (III) (2) was formed but in less than 35% yield. The products obtained

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the U. S. Government Synthetic Rubber Program.

by heating a dioxane solution were found to depend on the reflux period: after two to five hours a maximum yield (58%) of the cyclobutanone (III) was realized; after 48 hours a mixture made up of about equal parts of the cyclic ketone and of benzhydryl styryl ketone (IV) was formed, and after 96 hours the linear unsaturated ketone was the sole product. The identity of the linear ketone was established by comparing its properties with those of an authentic sample prepared by condensation of benzaldehyde with 1,1-diphenylacetone.

TABLE I

REACTION OF AZIBENZIL WITH STYRENE

SOLVENT	ADDITIVE	REACTION TIME (HRS.)	PRODUCT		
			Wt., g.	M.P., °C.	Approx. Composition
Acetone	—	38	1.7	132–136	100% TPCB[a]
Diethyl ether	—	41	0.5	132–136	100% TPCB[a]
Dioxane	—	42	.9	105–110	100% BSK[b]
Dioxane	Iodine, 2 crystals	24	1.7	134–138	100% TPCB
Dioxane	Copper powder, 0.01 g.	50	Three fractions:		
			0.6	129–136	67% TPCB
			.25	94–140	33% BSK
			.05	100–140	
Dioxane	Sulfuric acid, conc'd, 2 drops	48	1.6	132–137	100% TPCB
Dioxane	Triethylamine, 0.1 ml.	48	0.05	133–137	100% TPCB
Dioxane	—	1	1.4	134–137	100% TPCB
Dioxane	—	2	1.5	133–137	100% TPCB
Dioxane	—	5	1.7	134–137	100% TPCB
Dioxane	—	48	Three fractions:		
			0.65	95–125	50% TPCB
			.2	95–133	50% BSK
			.2	93–105	
Dioxane	—	96	1.5	93–105	100% BSK
Dibutyl ether	—	2	0.65	132–138	100% TPCB
Dibutyl ether	—	48	.6	106–112	100% BSK
o-Xylene	—	2	.65	133–137	100% TPCB
Dimethylformamide	—	48	—	—	—

[a] TPCB = 2,2,3-triphenylcyclobutanone.

[b] BSK = benzhydryl styryl ketone.

TABLE II

ATTEMPTED CONVERSION OF TRIPHENYLCYCLOBUTANONE TO BENZHYDRYL STYRYL KETONE

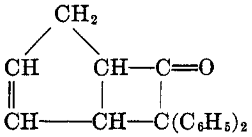
SOLVENT	REACTION TIME (HRS.)	PRODUCT	
		Wt., g.	M.P., °C.
Dioxane	96	1.25	128–137
Dibutyl ether	48	0.2	133–136
Dioxane	96	1.0	125–137[a]

[a] Azobis-α-isobutyronitrile (0.01 g.) added.

In the attempt to account for the formation of this unusual product, solutions of azibenzil and styrene in dioxane were heated in the presence of a variety of additives (Table I). It was observed that acid, iodine, and to a lesser degree copper powder, all of which facilitate the decomposition of aliphatic diazo compounds, promoted the formation of the cyclobutanone derivative. It was established by heating dioxane solutions of 2,2,3-triphenylcyclobutanone alone and in the presence of azobis-α-isobutyronitrile for 96 hours that conversion to the linear ketone cannot be effected by prolonged heating at the temperature of the azibenzil-styrene reaction nor by the addition of a free radical type catalyst (Table II). Staudinger did accomplish this conversion by employing a large excess of phenylmagnesium bromide (3), but no such reagent could be present in more than trace amounts in the azibenzil-styrene reaction. Thus the mechaism of the transformation remains obscure.

TABLE III

REACTION OF AZIBENZIL WITH OTHER OLEFINS AND STYRENE ANALOGS

OLEFIN[a]	REACTION TIME (HRS.)	PRODUCT	
		Yield, %	Structure
Cyclopentadiene	48	42	
p-Vinylbiphenyl	43	17	$(C_6H_5)_2CHCOCH{=}CH-C_6H_4C_6H_5(p)$
p-Methoxystyrene	96	24	$(C_6H_5)_2CHCOCH{=}CH-C_6H_4OCH_3(p)$
p-Methoxystyrene	2	—	—
p-Methoxystyrene[b]	5	—	—
p-Ethoxystyrene	96	29	$(C_6H_5)_2CHCOCH{=}CH-C_6H_4OC_2H_5(p)$
p-Ethoxystyrene	18	23	$(C_6H_5)_2CHCOCH{=}CH-C_6H_4OC_2H_5(p)$
p-Ethoxystyrene[c]	24	10	$(C_6H_5)_2CHCOCH{=}CH-C_6H_4OC_2H_5(p)$
p-Ethoxystyrene	2	—	—
p-Ethoxystyrene[b]	5	—	—
p-Ethoxystyrene[d]	24	—	—
p-Ethoxystyrene[e]	24	—	—

[a] No reaction occurred with the following compounds: β-bromostyrene, methyl cinnamate, methyl erucate, dodecene-1, 2-vinylpyridine, cyclohexene, 1,1-diphenylethylene, phenanthrene, 1,2-dihydronaphthalene, *o*-chlorostyrene, *m*-nitrostyrene, *p*-nitrostyrene, and 1-vinylnaphthalene. [b] Concentrated sulfuric acid (0.1 ml.) added. [c] Concentrated sulfuric acid (0.05 ml.) added. [d] A few iodine crystals added. [e] Acetone used as solvent.

In dibutyl ether and *o*-xylene the time required to produce only the linear ketone was less, but the yield was also lower. No solid product could be isolated when the reaction was carried out in dimethylformamide probably due to the basicity of the solvent since a similar result was observed in dioxane in the presence of triethylamine.

The action of azibenzil on a variety of other olefins and styrene analogs has been studied (Table III). Cyclopentadiene gave the same cyclobutanone derivative obtained by reaction with diphenylketene (4); in no case was it possible by altering the reaction conditions to produce an α,β-unsaturated ketone. Aliphatic olefins, cyclic monoölefins, and nuclear substituted styrene derivatives in which the substitution was of the *meta*-directing or ring-deactivating type did not enter into any reaction with azibenzil. Attempted reactions with 1-vinylnaphthalene and 2-vinylpyridine also failed. However, three *para*-substituted styrene derivatives in which the substitution was of the *ortho, para*-directing type yielded the corresponding α,β-unsaturated ketones in 17 to 29% yield, and no cyclobutanone derivative could be obtained.

EXPERIMENTAL

Azibenzil. The preparative procedure employed was that described in Organic Syntheses (5) except that the grinding step was omitted since it was found that the grinding of the dry reagents caused a violent reaction. Better than 90% yields of yellow to orange, crystalline products melting with decomposition at about 77–79° were obtained. The azibenzil could be stored for at least four weeks with very little decomposition over potassium hydroxide pellets in a desiccator in a refrigerator. The yields in the azibenzil-styrene reaction were shown to depend on the quality of the azibenzil, but the melting point did not appear to be a reliable criterion.

Reaction of azibenzil with styrene and other olefins. Except as indicated otherwise dioxane was the solvent employed, and a few crystals of trinitrobenzene were added to the reaction mixture to inhibit polymerization of the olefin. Experiments were carried out both under a nitrogen atmosphere and in the air, but it was demonstrated that the atmosphere had little or no effect on the reaction.

A solution of 2.2 g. (0.01 mole) of azibenzil and 0.01 mole of the olefin in 10 ml. of dioxane was heated under reflux. At the conclusion of the reflux period, the dioxane was removed under reduced pressure (water aspirator) while heating in a water-bath. After cooling to room temperature, about 25 ml. of ether was added. The ether solution was then gradually evaporated by sucking air over it, and a crude separation of the product was effected by collecting the several precipitates separately.

Unequivocal synthesis of benzhydryl styryl ketone. The condensation of 1,1-diphenylacetone (6) with benzaldehyde was effected using the exact amounts and procedure described by Staudinger and Rheiner (3). After recrystallization from 95% ethanol, yellow crystals, m.p. 108–110° were obtained.

Benzhydryl styryl ketone. The low melting azibenzil-styrene reaction product yielded after recrystallization from 95% alcohol faintly yellow needles, m.p. 110–112° and mixed melting point with the above product, 108–111°. The infrared absorption spectra of the two compounds were identical; absorption occurred at 1685 cm.$^{-1}$ which is in the range of a singly conjugated ketone carbonyl.[2]

Anal. Calc'd for $C_{22}H_{18}O$: C, 88.56; H, 6.08.

Found: C, 88.09; H, 5.91.

A solution of 0.552 mg. in 100 ml. of absolute ethanol showed a maximum absorption in the ultraviolet at a wavelength of 296 mμ with a molecular extinction coefficient of 22,900. This material also added bromine readily, gave a positive Baeyer's test, and slowly dissolved in concentrated sulfuric acid with the formation of a bright yellow color.

2,2,3-Triphenylcyclobutanone. The identity of the high melting azibenzilstyrene reaction product was established *via* melting point, mixed melting point, and infrared absorption spectra using for comparison an authentic sample prepared by reaction of diphenylketene with styrene. Absorption occurred at 1774 cm.$^{-1}$ which is in the range of a strained ketone carbonyl and may possibly be characteristic of a cyclobutanone.

Attempted conversion of 2,2,3-triphenylcyclobutanone to benzhydryl styryl ketone. A solu-

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[2] We are indebted to Miss Elizabeth M. Petersen for the infrared data and to Mr. J. O. Gardner for the ultraviolet data reported here.

tion of 1.5 g. of recrystallized triphenylcyclobutanone in 10 ml. of dioxane or dibutyl ether was heated under reflux in a nitrogen atmosphere, and the reaction product was handled in the same way as the azibenzil-olefin reaction product.

5,5-Diphenylbicyclo[3,0,2]-3-heptene-6-one. After recrystallization from 95% ethanol, the azibenzil-cyclopentadiene reaction product yielded white needles, m.p. 86–88°, which did not add bromine and gave a negative Baeyer's test. Infrared analysis showed absorption at 1772 cm.$^{-1}$ which is in the range of a strained ketone carbonyl and is comparable to that found for the 2,2,3-triphenylcyclobutanone (1774 cm.$^{-1}$).

Anal. Calc'd for $C_{19}H_{16}O$: C, 87.66; H, 6.20.

Found: C, 87.54; H, 6.29.

Benzhydryl p-phenylstyryl ketone. The azibenzil-*p*-vinylbiphenyl reaction product yielded after recrystallization from 95% ethanol a crystalline material, m.p. 149–154°, which did not add bromine but gave a positive Baeyer's test and an orange color in concentrated sulfuric acid. Infrared analysis showed absorption at 1685 cm.$^{-1}$, and a solution of 0.582 mg. in 100 ml. of absolute ethanol showed maximum absorption in the ultraviolet at a wave length of 323–326 mμ with a molecular extinction coefficient of 31,100.

Anal. Calc'd for $C_{28}H_{22}O$: C, 89.80; H, 5.92.

Found: C, 89.74; H, 6.10.

Benzhydryl p-methoxystyryl ketone. Recrystallization of the azibenzil-*p*-methoxystyrene reaction product from 95% ethanol yielded yellow needles, m.p. 129–131°, which added bromine, gave a positive Baeyer's test, and slowly dissolved in concentrated sulfuric acid with the formation of a strong yellow color. Infrared analysis showed absorption at 1684 cm.$^{-1}$, and a solution of 2.32 mg. in 100 ml. of absolute ethanol showed a maximum absorption in the ultraviolet at a wave length of 327–328 mμ with a molecular extinction coefficient of 22,300.

Anal. Calc'd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14.

Found: C, 84.38; H, 6.08.

Benzhydryl p-ethoxystyryl ketone. The azibenzil-*p*-ethoxystyrene reaction product was recrystallized from 95% ethanol and yielded white plates, m.p. 136–139°, which added bromine, gave a positive Baeyer's test, and developed a yellow color in concentrated sulfuric acid. Absorption in the infrared occurred at 1684 cm.$^{-1}$, and a solution of 1.92 mg. in 100 ml. of absolute ethanol showed a maximum absorption in the ultraviolet at a wave length of 328–331 mμ with a molecular extinction coefficient of 24,400.

Anal. Calc'd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48.

Found: C, 84.21; H, 6.51.

SUMMARY

The reaction of azibenzil with styrene can be carried out so that either 2,2,3-triphenylcyclobutanone or benzhydryl styryl ketone is the only product. Cyclopentadiene yields the same cyclobutanone derivative obtained by reaction with diphenylketene. *p*-Vinylbiphenyl, *p*-methoxystyrene, and *p*-ethoxystyrene under the same reaction conditions produce benzhydryl *p*-phenylstyryl ketone, benzhydryl *p*-methoxystyryl ketone, and benzhydryl *p*-ethoxystyryl ketone respectively.

URBANA, ILLINOIS

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