The substance in acetone solution did not decolorize aqueous permanganate; its solution in chloroform did not decolorize bromine in carbon tetrachloride. The compound was further characterized by its nmr spectrum at 40 Mc, peaks at $\tau$ 8.48 and 4.72 in $CDCl_3$[9]; ultraviolet spectrum in methanol, $\lambda_{max}$ 270 m$\mu$ ($\epsilon_{max}$ 136); and infrared spectrum in $CHCl_3$, 3080 (m) 3020 (w), 2960 (w), 1560 (sh), 1550 (s), 1462 (m), 1360 (s), 1297 (m), 1258 (w), 1054 (m), 972 (m), 945 (m), 928 (m), and 845 (w) cm$^{-1}$.

B.—The cycloelimination reaction was performed on 1,3-dinitro-1-bromo-2,2-dimethylpropane (20.0 g, 0.083 mole) by refluxing it 3 hr in a solution of 700 ml of absolute ethanol containing freshly fused potassium acetate (24.4 g, 0.244 mole). The crude product, obtained as a yellow oil from the chloroform extract, was placed on a 70-g Celite–silicic acid (1:3, 3 × 25 cm) column and, by means of a continuous extractor operated for 10 hr on petroleum ether (bp 30–60°), a crystalline material was eluted (3.0 g, 22%) that was identical with that described above. It was obtained in 34% yield when the reflux period was 30 min. There was no reaction in 40 hr at room temperature.

**Deuterium Exchange.**—Deuterium exchange was followed by nmr observations on the ratio of methyl to ring hydrogen peak areas in the recovered material as well as by the appearance of a C–D stretching frequency at 2280 cm$^{-1}$. The experiments were performed by mixing 3.00 ml of 0.07 $M$ potassium acetate in deuterium oxide with 5 ml of a 0.19 $M$ solution of the dinitro compound I in dioxane. The solutions were kept at 25.5° while protected from air and light. The extent of exchange after 44 hr, as estimated from peak areas, varied from 61 to 93% of completion for exchange of two hydrogens.

**Reaction with Formaldehyde.**—A mixture of I (0.320 g, 2.00 mmoles), paraformaldehyde (0.120 g, 4 mmoles), and potassium acetate (0.038 g, 0.39 mmole) in 30 ml of methanol became homogeneous after standing overnight and was allowed to stand for 18 days. The dinitrocyclopropane was recovered (0.308 g, 96%) unchanged. Under similar conditions, 2-nitropropane reacted to provide the known formaldehyde condensation product[10] in 60% yield.

**Action of Sodium Hydroxide.**—The dissolution of I (101 mg, 0.631 mmole) in 10% aqueous sodium hydroxide (2.37 g, 5.92 mmoles) occurred slowly on stirring for 1–1.5 hr, at room temperature, and I was not regenerated upon acidification with sulfuric acid at 0°. The organic product, extracted by chloroform (three 10-ml portions) and fractionated by liquid chromatography on 5 g of silicic acid–Supercel (3:1, 1 × 10 cm) with elution by benzene–petroleum ether (3:2), was a mixture consisting mainly of II (48 mg) with approximately 2 mg of III. These were characterized as indicated in the following sections. Nitrite ion was detected in the aqueous solution. When urea was added prior to acidification, and acidification was performed at 0° by addition of acetic acid–urea reagent,[11] only II was isolated. When nitrite ion, in fourfold excess, was added prior to acidification with glacial acetic acid at 0°, with subsequent warming to 25°, the product was almost exclusively III.

The action of sodium hydroxide in very dilute solutions was observed spectrophotometrically on aqueous solutions, 0.46 × $10^{-4}$ $M$ in I and in sodium hydroxide. In the first 2 min maxima were observed at 320 and 270 m$\mu$, but the latter was quickly obscured as the 320-m$\mu$ absorption increased to maximum intensity at about 25 min and thereafter gradually decreased. After 1.8 hr a maximum at 270 m$\mu$ could again be seen; at 22 hr the 320-m$\mu$ band was barely perceptible. Compound II with sodium hydroxide, each at 0.46 × $10^{-4}$ $M$, exhibited absorption, gradually decaying, at 320 m$\mu$.

**1,2-Dinitro-3-methyl-2-butene** (II).—The product from the acidification (12 ml of 20% aqueous acetic acid–urea) of alkaline solutions (25 ml of 0.124 $M$ NaOH) of I (511 mg, 3.19 mmoles) in the presence of urea (4.0 g, 67 mmoles) was obtained, after several short-path vacuum distillations, as a pale yellow liquid (375 mg, 75%) with a lachrymatory odor: bp 70° (1 mm); $n^{20}D$ 1.4972; $\lambda_{max}^{EtOH}$ 251 m$\mu$ ($\epsilon_{max}$ 5560); nmr, $\tau$ 7.71 (3), 7.51 (3), and 4.06 (2); infrared, 1648 (m), 1566 (s), 1525 (s), 1417 (m), 1368 (s), 1340 (s), and 889 (m) cm$^{-1}$.

*Anal.* Calcd. for $C_5H_8N_2O_4$: C, 37.50; H, 5.04; N, 17.49. Found: C, 37.63; H, 5.27; N, 17.40.

The compound darkens on standing and is largely decomposed in a period of one to several weeks depending upon the initial purity. It decolorizes aqueous permanganate instantly.

Ozonolysis of the compound (185 mg, 1.16 mmoles) in 50 ml of methylene chloride at −78°, with work-up by treatment with zinc dust followed by 2,4-dinitrophenylhydrazine reagent (229 mg, 1.16 mmoles), furnished acetone 2,4-dinitrophenylhydrazone (120 mg, 44%), mp 124.2°.

**3,4-Dinitro-5,5-dimethyl-2-isoxazoline** (III).—The product of acidification in the presence of nitrite ion was a colorless solid (194 mg from 337 mg of I) which could be purified by recrystallization from petroleum ether and sublimation: mp 97.0–97.2°; $\lambda_{max}^{alc}$ 268 m$\mu$ ($\epsilon_{max}$ 5910); nmr (40 Mc), $\tau$ 8.40 (double) and 4.36; infrared ($CHCl_3$), 1595, 1575, 1546, 1367, and 1015 cm$^{-1}$.

*Anal.* Calcd for $C_5H_7N_3O_5$: C, 31.75; H, 3.73; N, 22.22. Found: C, 31.84; H, 3.77; N, 22.13.

The absorption peaks at 1595 and 1575 cm$^{-1}$ agree well with literature reports[12] on a series of phenyl-substituted 2-isoxazolines.

There appeared to be no available data on the nitro-group frequency for the $-C(NO_2)=N-$ grouping. Accordingly, two known compounds were prepared and were found to exhibit nitro-group frequencies as follows: ethylnitrolic acid, $CH_3C(NO_2)=NOH$, mp 75–90°, lit[13] mp 81° dec, 1545 (s) and 1376 (m) cm$^{-1}$ in chloroform; and benzoylethylnitrolic acid, $CH_3C(NO_2)=N—OBz$, mp 132–135°, lit[14] mp 135°, 1555 (s) and 1375 (m) cm$^{-1}$ in chloroform. All data are thus consistent with the formulation of III as 3,4-dinitro-5,5-dimethyl-2-isoxazoline.

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# *cis-* and *trans-*1,3-Diphenylpropene

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The preparation and physical properties of *cis-* and *trans-*1,3-diphenylpropene are described, as is the ultraviolet photoisomerization of the *cis* into the *trans* isomer. Configurational assignments are made on the basis of infrared and nmr spectroscopy and by the relative rates of methoxylation–acetoxymercuration shown by the two isomers.

A compound, mp 57°, purported to be 1,3-diphenylpropene, was obtained in 1899 by Francis[2] as a by-product to the $\alpha$-ethylation of 1,3-diphenyl-2-propanone with ethyl iodide and sodium ethoxide, followed by atmospheric-pressure distillation of the crude product. The compound produced a dibromide, mp 231°, on bromination in benzene solution. A second compound designated as 1,3-diphenylpropene was prepared by Dieckmann and Kämmerer[3] in

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[1] NSF Science Teaching Faculty Fellow, 1962–1963.

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1906 by several methods, including (1) the dehydrobromination and decarboxylation of β-bromo-α-benzyl-β-phenylpropionic acid with soda lime; (2) the dehydration of 1,3-diphenyl-1-propanol and the dehydrochlorination of 1-chloro-1,3-diphenylpropane; (3) the dehydration of 1,3-diphenyl-2-propanol and the dehydrochlorination of 2-chloro-1,3-diphenylpropane; and (4) the debromination of 1,2-dibromo-1,3-diphenylpropane with zinc. The Dieckmann–Kämmerer product was an oil, bp 178–179° (15 mm), which afforded a crystalline dibromide, mp 110°, on bromination in chloroform. The authors supported its structure by permanganate oxidation to benzoic and phenylacetic acids, and suggested that it was a geometrical isomer of Francis' compound. Since then, the Dieckmann–Kämmerer isomer, usually characterized as its dibromide (mp 110°), has been prepared by a variety of methods,[4-27] the most convenient of which is the aldol condensation, dehydration, and deformylation of phenylacetaldehyde with alcoholic potassium hydroxide,[5,18,27] a procedure originated by Stoermer, Thier, and Laage[5] in 1925.

In 1947 Tuot and Guyard[28] reported the preparations of what were purportedly the *trans* (mp 51°) and the *cis* (oil, $n^{20}$D 1.5807) isomers of 1,3-diphenylpropene by the dehydrations of 1,3-diphenyl-2-propanol and 1,3-diphenyl-1-propanol, respectively, with sulfuric acid. The configurational assignments of these authors are supported by no experimental data, however, nor indeed are the structures of their products (or precursors) confirmed even by elemental analyses or the preparation of derivatives. In contrast, Beaven and Johnson[18] have argued, on the basis of its gas chromatographic behavior, and Bokadia and co-workers,[24] on the basis of its infrared spectrum (ν 963 cm$^{-1}$, *trans*-CH=CH—), that the Dieckmann–Kämmerer product (dibromide mp 110°) must be the *trans* isomer. More recently Zbiral[26] has prepared the Dieckmann–Kämmerer isomer by the action of phenylmethylenetriphenylphosphorane on epoxystyrene, claiming with some amazement but with no experimental support that the olefin product had exclusively the *cis* configuration. In the same year (1963), Gossaver, Morcillo, and Perez-Ossorio[27] argued, again on the basis of infrared spectroscopy, that the Dieckmann–Kämmerer product possessed the *trans* configuration, and that another isomer, prepared by the partial reduction of of 1,3-diphenylpropyne was the authentic *cis* product.

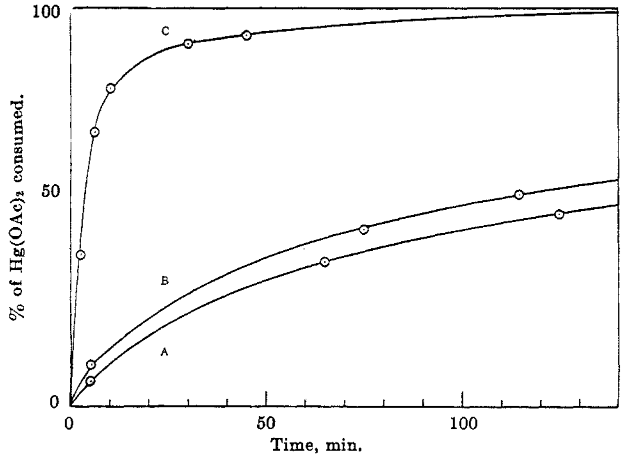

Figure 1.—Methoxylation–acetoxymercuration rate curves for (A) *trans*-PhCH$_2$CH=CHPh, $t_{1/2}$ = 133 min; (B) *cis*-PhCH$_2$CH=CHPh, $t_{1/2}$ = 96 min; and (C) PhCH$_2$C≡CPh, $t_{1/2}$ = 3.5 min.

The literature involving the configurations, and in some instances even the identities, of the isomeric 1,3-diphenylpropenes is thus confusing. In connection with another problem wherein these isomers arose as primary products, it has been necessary for us to prepare authentic samples of each isomer and to characterize them by unambiguous means.

Repetition of the procedure of Stoermer, Thier, and Laage produced crude 1,3-diphenylpropene in 91% yield. Purified by chromatography and successive recrystallization, the product, homogeneous on thin layer chromatography (tlc), had mp 18° and $n^{24}$D 1.5985. Its *trans* geometry was confirmed by a strong infrared band at 966 cm$^{-1}$, and by C-1 and C-2 vinyl protons appearing in the nmr spectrum at 6.40 and 6.25 ppm, respectively, with a *trans* coupling constant of 16 cps. Accompanying the formation of *trans*-1,3-diphenylpropene by this preparation was a small quantity of α,γ-diphenyl-β-benzyl-δ-valerolactone, mp 162.5–163.5°.

1,3-Diphenylpropyne was prepared by the procedure of Johnson, Jacobs, and Schwartz.[29] Its hydrogenation in the presence of Lindlar catalyst[30] yielded a product whose gas chromatography (gc) behavior showed it to consist of 85% *cis*- and 9% *trans*-1,3-diphenylpropene. The former isomer could be prepared more conveniently by irradiation of the latter (dissolved in benzene containing acetophenone) with ultraviolet light, whereby a 1:1 mixture of the two isomers could be readily obtained. Separated by gc, the pure *cis* isomer had $n^{29}$D 1.5850 and showed no 966-cm$^{-1}$ infrared absorption band. The nmr spectrum showed the C-1 and C-2 vinyl protons as pairs of triplets centered, re-

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spectively, at 6.52 and 5.82 ppm, with a *cis* coupling constant of 11.5 cps.

The above configurational assignments were confirmed by the relative rates of reaction of each isomer with mercuric acetate in methanol.[31] The *cis* isomer underwent methoxylation–acetoxymercuration at a typically[31] faster rate ($t_{1/2}$ = 96 min) than the *trans* isomer ($t_{1/2}$ = 133 min). Each isomer, as well as 1,3-diphenylpropyne, afforded identical samples of 1,3-diphenylpropane on hydrogenation with 30% Pd–C catalyst. *cis*-1,3-Diphenylpropene proved to run ahead of the *trans* isomer both in thin layer and vapor phase chromatography.

Finally, we have attempted to prepare Francis' hydrocarbon, mp 57°, by repeating his conditions[2] for the ethylation of 1,3-diphenyl-2-propanone. 1,3-Diphenyl-2-pentanone (oxime mp 89.5°) was readily obtained by his procedure, but in our hands the 57° hydrocarbon was not forthcoming. Similarly, the action of sodium ethylate alone on 1,3-diphenyl-2-propanone yielded a small amount of α-hydroxy-α,β-diphenylpropionic acid, mp 168–168.5°, as the only crystalline product, with none of the desired 57° hydrocarbon. It seems conceivable to us, therefore, that Francis' product may have been an impure sample of *trans*-stilbene (mp 124°), formed by dehydration and decarboxylation of the above α-hydroxy-α,β-diphenylpropionic acid during distillation. This suggestion is reasonable in that *trans*-stilbene dibromide has mp 237°, whereas the dibromide from Francis' hydrocarbon had mp 231°.

## Experimental Section

***trans*-1,3-Diphenylpropene.**—This alkene was prepared by heating phenylacetaldehyde (30.0 g) and potassium hydroxide (15.0 g) in refluxing ethanol (105 ml) after the method of Stoermer, Thier, and Laage.[5] After 4 hr the mixture was cooled, diluted with 500 ml of water, and extracted with ether. The extract was washed with 10% sodium hydroxide solution and with water, then dried ($MgSO_4$), filtered through Norit, and evaporated to yield 22.2 g (91.5%) of crude *trans*-1,3-diphenylpropene, a thin oil. Tlc (silica gel, hexane) showed the presence of two minor impurities, but none of the *cis* isomer. The product was purified by chromatographing on a 20 × 160 mm column of alumina (hexane eluent), concentrating, and recrystallizing five times from hexane (chilling in Dry Ice–2-propanol). The purified product, stripped of residual solvent and homogeneous on tlc, was a colorless oil, mp 18°, $n^{24}\text{D}$ 1.5985. The *trans* geometry was confirmed by the presence of strong infrared absorption at 966 $cm^{-1}$, a band characteristic of the "wagging" of an ethylenic C–H bond in the *trans* position,[32,33] and by nmr spectroscopy.[34] The nmr spectrum (100 Mc) showed a ten-proton multiplet between δ 6.9 and 7.5 for the aromatic protons, and a two-proton doublet centered at δ 3.48 for the benzylic protons. The C-1 vinyl proton appeared at δ 6.40 and the C-2 vinyl proton at δ 6.25, with a *trans* coupling constant[35] of 16 cps. The C-2-vinyl proton was coupled with the benzylic protons with a coupling constant of 5 cps. The ultraviolet spectrum (hexane) showed $\lambda_{max}$ 252 mμ (log ε 4.39) in agreement with the spectrum described by Gossauer, Morcillo, and Perez-Ossorio.[27]

The above 10% aqueous NaOH solution was acidified and extracted with ether. The extract was washed, dried, and evaporated to yield 1.89 g of thick oil, which slowly crystallized. The material was recrystallized three times from 2-propanol, then dried *in vacuo* to give 0.33 g of α,γ-diphenyl-β-benzyl-δ-valerolactone, mp 162.5–163.5°.

*Anal.* Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47; mol wt, 342.4. Found: C, 84.24; H, 6.44; mol wt, 341 (vapor pressure osmometer).

The nmr spectrum (60 Mc) showed approximately 15 aromatic protons between δ 6.9 and 7.5, a two-proton $CH_2$ doublet centered at δ 4.78 with a coupling constant of 6 cps, a one-proton α-benzylic H doublet centered at δ 3.78 with a coupling constant of 7 cps, a one-proton γ-benzylic H pair of triplets centered around δ 3.37, and a one-proton multiplet around δ 2.6–2.7 corresponding to the β-proton, upon which was superimposed a perturbed doublet centered at δ 2.5 corresponding to the $CH_2$ protons. The nmr spectrum was unchanged after treatment with neutral $D_2O$, showing the expected absence of exchangeable protons. The C=O stretching frequency of the lactone appeared at 1720 $cm.^{-1}$

***cis*-1,3-Diphenylpropene.**—1,3-Diphenylpropyne was prepared by the action of phenylethynylmagnesium bromide on benzyl *p*-toluenesulfonate,[36] after the procedure of Johnson, Jacobs, and Schwartz.[29] The product, which was purified by elution (petroleum ether) from a column of silica gel G, was homogeneous on gc, had $n^{29}\text{D}$ 1.6008, and readily absorbed 2 moles of hydrogen on catalytic hydrogenation, producing a sample of 1,3-diphenylpropane whose infrared spectrum was identical with that of an authentic sample.

A solution of pure 1,3-diphenylpropyne (6.20 g) in hexane (30 ml) was stirred under hydrogen (1 atm, 28°) in the presence of Lindlar's catalyst[30] (1.5 g) until the absorption of hydrogen ceased (741 cc, 94.1%). Examination of the product by gc showed it to be made up of approximately 85% *cis*-1,3-diphenylpropene, 9% of the *trans* isomer, and 6% of starting material. The pure *cis* isomer was isolated by gc [$^3/_8$ × 20 in. column of 5% silicone gum rubber (Wilkins SE-30)] and showed $n^{29}\text{D}$ 1.5850, $\lambda_{max}^{cyclohexane}$ 242 mμ (log ε 4.20). With the exception that it contained two small, extraneous absorption bands at 1550 and 1655 $cm^{-1}$, the infrared spectrum of this sample was identical in all respects with that of the sample of *cis*-1,3-diphenylpropene prepared below.

**Conversion of *trans*- into *cis*-1,3-Diphenylpropene.**—A solution of the above *trans*-1,3-diphenylpropene (9.0 g) in benzene (9 ml) containing acetophenone[37] (2 ml) was placed in a Rayoner photochemical reactor (The Southern N. E. Ultraviolet Co., Middletown, Conn.) and irradiated for 22.5 hr with 2537-A ultraviolet light. Examination of the reaction mixture by gc showed it to contain the *cis* and *trans* olefins in about a 1:1 ratio. The benzene and acetophenone were mainly removed at 100° *in vacuo* with a rotary evaporator, and the residue was distilled through a heated 8-in. column containing a stainless steel packing. The first fraction [1.14 g, bp 103–104° (1 mm)] contained 69% *cis* isomer by gc analysis, and pure *cis*-1,3-diphenylpropene was isolated as above by preparative gc, $n^{29}\text{D}$ 1.5850.

*Anal.* Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.70; H, 7.46.

The infrared spectrum of the *cis* isomer was quite similar to that of the above *trans* isomer in the region from 4000 to 1000 $cm^{-1}$. Below 1000 $cm^{-1}$, it lacked the strong 966-$cm^{-1}$ band characteristic of the *trans* isomer, and displayed instead a moderately strong band at 920 $cm^{-1}$ and a strong band at 772 $cm^{-1}$. The nmr spectrum (60 Mc) of the *cis* isomer displayed ten aromatic protons as two bands centered at δ 7.2, the two benzylic C-3 protons as a pair of doublets centered at δ 3.62, the C-1 vinyl proton as a pair of triplets centered at δ 6.52, and the C-2 vinyl proton as a pair of triplets centered around δ 5.82. The C-1 and C-2 vinyl protons were coupled with a *cis* coupling constant[35] of 11.5 cps, while the coupling constant between the C-2 and C-3 protons was 7.5 cps. A long-range coupling constant of 1.5 cps existed between the C-1 and C-3 protons.

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**Methoxylation–Acetoxymercuration Rates.**—The rates of methoxylation–acetoxymercuration of *cis*- and *trans*-1,3-diphenylpropene and of 1,3-diphenylpropyne were determined at room temperature by the procedure of Wright and co-workers.[31] Typically, about 1 mmole of the hydrocarbon was dissolved in absolute methanol ($x$ ml), and the solution was treated with $x$ ml (1 equiv) of a 0.20 $M$ solution of mercuric acetate in absolute methanol. Aliquots of 1 ml were removed at successive time intervals and quenched in water (20 ml) containing 1 ml of saturated potassium nitrate solution, 0.05 $M$ in nitric acid. The mixture from each aliquot was extracted five times with 3-ml portions of chloroform (discarded), and the aqueous layer was rinsed (5 ml of water) into a 125-ml flask and treated with 1 ml of indicator solution (saturated ferric ammonium sulfate in 0.5 $M$ nitric acid). Unchanged mercuric acetate was determined by titration with 0.05 $M$ potassium thiocyanate solution. The resulting rate data are plotted in Figure 1.

**Catalytic Hydrogenation of *cis*- and *trans*-1,3-Diphenylpropene.**—A sample of *trans*-1,3-diphenylpropene (5.15 mmoles) in ethanol (25 ml) was catalytically reduced at atmospheric pressure in the presence of 30% palladium–charcoal (0.1 g) whereupon 5.29 mmoles of hydrogen was consumed. Similar reductions, involving the expected hydrogen uptake, were conducted with *cis*-1,3-diphenylpropene and 1,3-diphenylpropyne. The 1,3-diphenylpropane products from each reduction had identical infrared and ultraviolet spectra, showed identical retention times on gc, and had $n^{29}\mathrm{D}$ 1.5558. Bromination of *trans*-1,3-diphenylpropene in chloroform solution led to the dibromide described by Dieckmann and Kämmerer,[3] mp 107–109.5°.

**Ethylation of 1,3-Diphenyl-2-propanone.**—In attempt to prepare the hydrocarbon product, mp 57°, obtained by Francis,[2] the following duplication of his experiment was attempted. Freshly crystallized 1,3-diphenyl-2-propanone (10.00 g, mp 34–34.5°) was dissolved in absolute ethanol (40 ml) and treated with sodium (1.20 g, 1.1 molar equiv) in absolute ethanol (20 ml). The yellow solution was treated with freshly distilled ethyl iodide (8.90 g, 1.2 molar equiv) in absolute ethanol (10 ml) and the mixture was heated under reflux for 2.25 hr, then allowed to stand 18 hr, and poured into water. The mixture was extracted with ether, acidified, and reextracted three times with ether. The combined extracts were washed with 10% aqueous sodium hydroxide, dried, and stripped of solvent, yielding 10.73 g (94.7%) of crude 1,3-diphenyl-2-pentanone as a thin, yellow oil. Tlc (silica, benzene) revealed that the crude product contained some unchanged starting material. The product was characterized as its oxime, which was recrystallized twice from ethanol, mp 89.5°.

*Anal.* Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.44; H, 7.51; N, 5.53.

The nmr spectrum (60 Mc) accorded with the indicated structure: hydroxyl proton, $\delta$ 9.13; aromatic protons, $\delta$ 7.23; C-1 benzylic protons, pair of doublets centered, respectively, at $\delta$ 4.12 and 3.06 with a coupling constant of 14.5 cps; C-3 proton, pair of doublets centered at $\delta$ 3.28 with coupling constants of 7 and 9 cps; C-4 methylene protons, multiplet centered at $\delta$ 1.85; C-5 methyl protons, multiplet centered at $\delta$ 0.73, coupling constant 7.5 cps. This oxime has been previously reported as having mp 106[2] and 96–97°.[38] It is possible that either polymorphism or geometrical configuration may be responsible for the melting point discrepancies noted.

The bulk of the crude material was distilled at atmospheric pressure. About half showed bp 315–319°, and the remainder foamed too badly to continue. Neither the distillate nor residue deposited crystals on standing for 9 months.

Acidification of the above 10% aqueous alkali wash, followed by extraction with ether, gave a trivial quantity (0.05 g) of acidic material, an amber oil.

**Action of Sodium Ethoxide on 1,3-Diphenyl-2-propanone.**—A second attempt to obtain Francis' 57° hydrocarbon was made as follows. A mixture of 1,3-diphenyl-2-propanone (10.0 g) and sodium (1.10 g) dissolved in absolute ethanol (70 ml) was heated under reflux for 24 hr, poured into water, and processed as above. The neutral product (10.3 g) was a thick amber oil. About half of it distilled with decomposition at 330–333°. Neither the distillate nor residue crystallized on standing during 9 months. The acidic product (0.2 g) crystallized on standing, and was recrystallized from benzene. It was found by analysis, melting point (168–168.5°), and nmr spectrum to be $\alpha$-hydroxy-$\alpha$,$\beta$-diphenylpropionic acid.

*Anal.* Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.83. Found: C, 74.45; H, 5.93.

The nmr spectrum (60 Mc) showed 12 protons in the $\delta$ 7–7.8 region, indicating that the OH and COOH protons were buried under the ten phenyl protons. The benzylic protons were nonequivalent, as indicated by their appearance as a pair of doublets centered, respectively, at $\delta$ 3.22 and 3.60, with a coupling constant of 13.5 cps.

This compound has been reported to have mp 165–166° and to be preparable by passing air through an alkaline solution of 1,3-diphenyl-2-propanone at 70°.[39,40]

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# Cyclopropylpyridines. Synthesis and Electronic Interaction[1]

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Carbalkoxy- and cyano-substituted cyclopropylpyridines have been synthesized in two ways: (a) by treatment of the appropriate vinylpyridine with ethyl diazoacetate, and (b) by treatment of 4-picolyl chloride with an acrylate ester or acrylonitrile and sodium hydride in the cold. Gas chromatographic and n.m.r. spectral examination of the products shows that both processes lead to a mixture of the *cis* and *trans* isomers with the *trans* predominating, but that the latter reaction is somewhat more stereoselectively *trans*. The products have been converted to $\alpha$,$\alpha$-disubstituted pyridylcyclopropanemethanols by Grignard reactions. The unsubstituted parent system, 4-cyclopropylpyridine, has been obtained in good yield by treatment of 4-pyridylpropyltrimethylammonium chloride with sodamide. Inspection of the ultraviolet and infrared spectra and of the dissociation constants of various of the cyclopropylpyridine derivatives provides evidence of electronic interaction between the cyclopropane and pyridine ring systems. *trans*-2-(4-Pyridyl)-$\alpha$,$\alpha$-diphenylcyclopropanemethanol, but not the *cis* isomer, has been found to have interesting psychopharmacological properties.

In continuing study of the chemical properties and pharmacological actions on the central nervous system of substituted, particularly 4-substituted, pyridine derivatives,[2] we became interested in ascertaining the effect of attaching a cyclopropane ring directly to the pyridine nucleus. Compounds having such an arrangement could be expected to display properties

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