The distillate obtained by acidification and distillation of the filtrate was neutralized with 10% sodium hydroxide solution and evaporated to dryness. The sodium salt obtained was converted into the *p*-bromophenacyl ester which melted at 84.5–85°. The melting point of *p*-bromophenacylacetate recorded in the literature is 84.5–85°.

**β-Methoxy-α-naphthoylacetone.**—2-Methoxy-1-acetonaphthone was converted into β-methoxy-α-naphthoylacetone by the method of Wittig and Blumenthal.[10] The yield of the colorless solid melting at 71–72.5° was 41.3% of the theoretical amount.

**The Reaction of β-Methoxy-α-naphthoylacetone with Sodium Hypobromite.**—Five grams of the diketone in 300 cc. of cold 10% alkali was added to a hypobromite solution containing 7.2 cc. of bromine in 150 cc. of cold 10% alkali. Eight grams of solid was obtained after twenty-four hours stirring. The compound after recrystallization from methanol melted at 136–137°, and was shown by the mixed melting point method to be 1-tribromoacetyl-2-methoxynaphthalene.[2] No bromoform or carbon tetrabromide was obtained.

## Summary

The action of hypobromite solutions on β-diketones of the type $ArCOCH_2COCH_3$ has been shown to take the course represented by the equations

$$ArCOCH_2COCH_3 + 2NaOBr \longrightarrow ArCOCBr_2COCH_3 + 2NaOH \quad (1)$$
$$ArCOCBr_2COCH_3 + NaOH \longrightarrow ArCOCHBr_2 + CH_3CO_2Na \quad (2)$$
$$ArCOCHBr_2 + NaOBr \longrightarrow ArCOCBr_3 + NaOH \quad (3)$$
$$ArCOCBr_3 + NaOBr \longrightarrow ArCO_2Na + CBr_4 \quad (4)$$

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[10] Wittig and Blumenthal, *Ber.*, **60B**, 1085 (1927).

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

# The Addition of Free Radicals to Certain Dienes, Pyrrole and Maleic Anhydride

BY J. B. CONANT AND BACON F. CHOW

In a preliminary paper,[1] it was shown that the free radical, triphenylmethyl, combines with isoprene and 2,3-dimethylbutadiene-1,3, addition taking place in the 1 and 4 positions. We have now extended the study of this reaction to include a number of unsaturated compounds and two other free radicals, namely, phenylxanthyl and benzylxanthyl. Both of these radicals combined with isoprene, although in the case of the slightly dissociated benzyl compound,[2] no reaction was evident at room temperature after seven days; in both cases the best yield was obtained by heating the two compounds at 100° for twenty-four hours. Since phenylxanthyl is much less associated than triphenylmethyl and benzylxanthyl much more so, it is evident that the reaction between a butadiene and a dissociable ethane does not depend on the degree of dissociation.

Triphenylmethyl was allowed to interact with butadiene-1,3 and pentadiene-1,3 (piperylene). The addition reaction proceeded in both cases at

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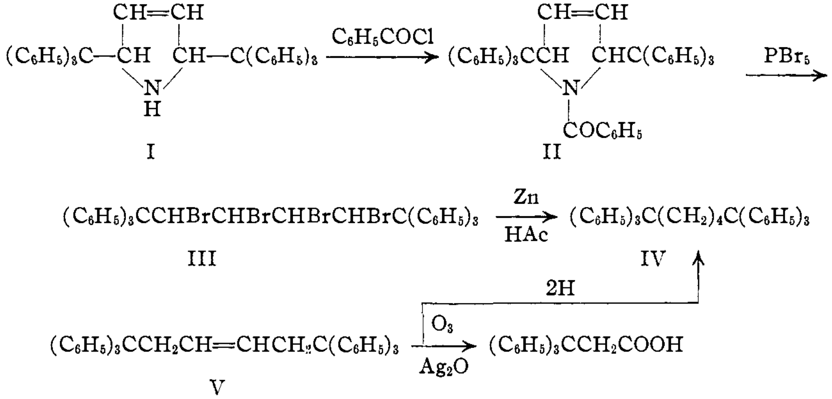
[1] THIS JOURNAL, **53**, 1941 (1931).

[2] *Ibid.*, **47**, 572 (1925).

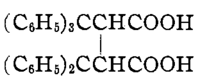
room temperature. Since in piperylene one of the terminal atoms of the conjugated system carries a methyl group, it is clear that the presence of at least one such group does not interfere seriously with the reaction.

Pyrrole combines rapidly with triphenylmethyl; a 60% yield of the addition product can be obtained after a few hours at room temperature. The structure of the product (I) was established by benzoylating and treating the benzoyl derivative with phosphorus pentabromide. The tetrabromide (III) thus formed could be reduced to a saturated hydrocarbon (IV) identical with that obtained by the catalytic reduction of (V), the addition product of triphenylmethyl to butadiene. The position of the triphenylmethyl groups in V was shown by its oxidation to the known β-triphenylpropionic acid.



The structure of I is rigorously established by these transformations except for the position of the double linkage. Further evidence as to the structure follows from the fact that the compound is a secondary amine (its basic properties are evident from the fact that it dissolves in concentrated hydrochloric acid, in spite of its extreme insolubility in water and alcohol). An addition product between triphenylmethyl and 2,4-dimethylpyrrole has also been prepared. Presumably this substance has a structure analogous to I but this as yet has not been proved. It is worthy of note that pyrrole behaves toward triphenylmethyl like a diene, whereas the reaction of pyrrole with maleic anhydride takes an unusual course.[3]

A reaction between triphenylmethyl and maleic anhydride occurs when a benzene solution of the two components is heated for some hours. The chief product which can be isolated from the reaction mixture is a dibasic acid, and its anhydride. The analyses, titration and molecular weight of this anhydride, acid and ester indicate quite clearly that the acid is α,β-di-(triphenylmethyl) succinic acid (VI). It evidently is formed by the ad-



$$\begin{matrix}(C_6H_5)_3CCHCOOH\\ |\\ (C_6H_5)_2CCHCOOH\end{matrix}$$

VI

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[3] Diels, *Ann.*, **490**, 201 (1931).

dition of triphenylmethyl to the very reactive double linkage in maleic anhydride. This reaction thus affords additional evidence of the pronounced unsaturation of the carbon–carbon double linkage in maleic anhydride. It is interesting that triphenylmethyl adds to both a diene and maleic anhydride—two substances which combine together in the Diels reaction.

## Experimental

**1,4-(Phenylxanthyl)-2-methylbutene-2,** $O(C_6H_4)_2C(C_6H_5)CH_2C(CH_3){=}CHCH_2C(C_6H_5)C(C_6H_4)_2O$.—Dry solid diphenyldixanthyl prepared from 5 g. of phenylxanthanol by reduction with chromous chloride, was dissolved in 20 cc. of isoprene in nitrogen. After heating for twenty-four hours at 100°, the isoprene was distilled and the residue purified by crystallization from acetone after removal of a certain amount of peroxide which was insoluble in ether. The yield was 1.2 g. (23%). In another experiment in which the reaction mixture stood at room temperature for seven days the yield was 5%. The compound melted at 249–250°.

*Anal.* Calcd. for $C_{43}H_{34}O_2$: C, 88.6; H, 5.88. Found: C, 88.3, 88.4; H, 6.1, 6.2.

*Mol. wt.* (Freezing point in benzene). Calcd., 582. Found: 540, 514.

**1,4-(Benzylxanthyl)-2-methylbutene-2,** $O(C_6H_4)_2C(CH_2C_6H_5)CH_2C(CH_3){=}CHCH_2C(CH_2C_6H_5)(C_6H_4)_2O$.—A solution of 4 g. of dibenzyldixanthyl in 30 cc. of isoprene was heated to 100° for twenty-four hours. The product was obtained by adding petroleum ether to the reaction mixture; it was recrystallized from ether. The yield was 2 g. (45%). The compound melted at 218°.

*Anal.* Calcd. for $C_{45}H_{38}O_2$: C, 88.5, H, 6.3. Found: C, 88.6, 88.7; H, 6.5, 6.5.

*Mol. wt.* (By freezing point in benzene). Calcd., 610. Found: 550, 583.

**1,4-(Triphenylmethyl)-butene-2,** $(C_6H_5)_3CCH_2CH{=}CHCH_2C(C_6H_5)_3$.—A 10% yield of this compound was obtained by allowing a solution of 5 g. of hexaphenylethane and 1 g. of butadiene in 30 cc. of benzene–toluene mixture to stand at room temperature thirty-six hours in nitrogen. The product was recrystallized from benzene–petroleum ether; it melted at 224°.

*Anal.* Calcd. for $C_{42}H_{36}$: C, 93.3, H, 6.7. Found: C, 93.0, 92.8; H, 6.7, 6.8.

*Mol. wt.* (In freezing benzene). Calcd., 540. Found: 480, 497.

Oxidation.—The hydrocarbon was ozonized in the usual manner in carbon tetrachloride solution and the product further oxidized by boiling in methyl alcohol with silver oxide. The acid material thus formed was isolated in the usual fashion and shown to be β-triphenylpropionic acid by a mixed melting point; the yield of acid was 32%.

**1,4 - (Triphenylmethyl) - 1 - methylbutene - 2,** $(C_6H_5)_3CCH(CH_3)CH{=}CHCH_2C(C_6H_5)_3$.—Two grams of piperylene and 8 g. of hexaphenylethane were dissolved in 20 cc. of benzene. After allowing the reaction mixture to stand for three days in nitrogen, the solvent and excess piperylene were removed by distillation. After filtering off the peroxide which was insoluble in ether, the product crystallized from ether. It melted after recrystallization at 174°; the yield was 19%.

*Anal.* Calcd. for $C_{43}H_{38}$: C, 93.1; H, 6.9. Found: C, 92.8, 92.6; H, 6.7, 7.0.

*Mol. wt.* (In freezing benzene). Calcd., 554. Found: 472, 464.

**2,5-(Triphenylmethyl)-2,5-dihydropyrrole (Formula I).**—A solution of 8 g. of triphenylmethyl and 3.5 g. of pyrrole in benzene was allowed to stand in nitrogen for several hours. The product was isolated in the usual manner after removing 1 g. of peroxide. A crude dark gray product weighing 4.5 g. (60% yield) was obtained. Repeated recrystallization from benzene with the aid of charcoal yielded a colorless compound which melted with decomposition at 250°. The compound was soluble in concentrated aqueous hydrochloric and glacial acetic acid but insoluble in ethyl alcohol.

*Anal.* Calcd. for $C_{42}H_{35}N$: C, 91.9; H, 6.4. Found: C, 91.4, 91.7; H, 6.3, 6.4. *Mol. wt.* (Freezing benzene). Calcd., 553. Found: 520, 481.

**1-Benzoyl-2,5-(triphenylmethyl)-2,5-dihydropyrrole.**—The dihydropyrrole was benzoylated in a benzene solution with benzoyl chloride and aqueous sodium hydroxide. A 21% yield was obtained. The product melted at 265–266° and was insoluble in concentrated hydrochloric acid.

*Anal.* Calcd.: C, 89.5; H, 6.0. Found: C, 89.2, 89.4; H, 6.2, 6.2. *Mol. wt.* (Freezing benzene). Calcd., 655. Found: 571, 580.

**1,4-(Triphenylmethyl)-1,2,3,4-tetrabromobutane.**—A solution of the benzoyl compound in benzene (0.5 g. in 10 cc.) was treated with 1.5 g. of phosphorus tribromide and 0.8 g. of liquid bromine. The mixture was heated and the phosphorus oxybromide and benzonitrile distilled off *in vacuo*. After decomposing with water and alkali a black solid was obtained which was purified by extracting its ether solution with aqueous sodium hydroxide and 50% sulfuric acid. A purple impurity passed into the aqueous acid. The product was obtained from the ether layer as an almost colorless solid of m. p. 168° (15% yield). A qualitative test showed the absence of nitrogen.

*Anal.* Calcd. for $C_{42}H_{34}Br_4$: C, 58.8; H, 4.0; Br, 37.3. Found: C, 58.3, 58.6; H, 4.1, 4.3; Br, 37.9.

**1,4-(Triphenylmethyl)-butane.**—The product obtained by the catalytic hydrogenation of 1,4-triphenylbutene-2 with Adams catalyst (80% yield) melted at 189° after recrystallizing from ether–petroleum ether. The same substance was obtained from the tetrabromide mentioned above by heating it in 90% acetic acid with zinc dust for seven hours at 100°. The identity of the two samples was shown by a mixed melting point.

*Anal.* Calcd. for $C_{42}H_{38}$: C, 93.0; H, 7.0. Found: C, 92.4; H, 6.8.

**Addition Product of 2,3-Dimethylpyrrole and Triphenylmethyl.**—A benzene solution of 3 g. of 2,4-dimethylpyrrole and the triphenylmethyl from 5 g. of triphenylmethyl chloride was heated in nitrogen at the boiling point for six hours. After exposure to air, 1 g. of peroxide was isolated and 1.5 g. of black solid material melting at 190–204°. By repeated crystallization from benzene with the use of charcoal a white solid melting at 227° was obtained (yield 0.5 g.).

*Anal.* Calcd. for $C_{43}H_{37}N$: C, 91.0; H, 6.6; N, 2.5. Found: C, 90.7; H, 6.7; N, 1.7.

**α,β-Di-(triphenylmethyl)-succinic Acid.**—Forty grams of maleic anhydride was added to a benzene solution (200 cc.) of hexaphenylethane prepared by action of molecular silver on 120 g. of the chloride. The solution was boiled in nitrogen for several hours and then exposed to air; no peroxide was formed, showing a conversion of the free radical. The reaction mixture was extracted several times with 3% sodium hydroxide, and an insoluble sodium salt formed at the interface. This and the aqueous extracts were acidified and transferred to ether and crystals obtained in the usual manner; yield 60 g., m. p. 142–145°; recrystallized from glacial acetic acid, m. p. 148° with decomposition.

*Anal.* Calcd. for $C_{42}H_{32}O_4$: C, 84.0; H, 5.4; equiv. wt., 300. Found: C, 84.6; H, 5.9, 5.6. *Equiv. wt.* by titration, 295.

**Dimethyl Ester.**—A portion of the acid was esterified by the action of diazomethane on a dry ether solution. In this way a crystalline compound melting at 212–213° was obtained.

*Anal.* Calcd. for $C_{44}H_{32}O_4$: C, 84.1; H, 5.8. Found: C, 84.1; 83.9; H, 6.0, 6.1.

**α,β-Di-(triphenylmethyl)-succinic Anhydride.**—The residue from the original reaction mixture after extracting with sodium hydroxide was evaporated to dryness and recrystallized from acetone. A crystalline material melting at 232° was obtained (yield 12 g.).

*Anal.* Calcd. for $C_{42}H_{30}O_3$: C, 86.2; H, 5.5. Found: C, 86.5, 86.3; H, 5.6, 5.3.

When a sample of the anhydride was boiled with alcoholic sodium hydroxide and the solution acidified, the di-triphenylmethylsuccinic acid was formed. It was identified by conversion to the dimethyl ester whose melting point is more satisfactory.

## Summary

Triphenylmethyl and benzylxanthyl have been found to add in the 1,4 position to certain 1,3-dienes and pyrrole. Two molecules of triphenylmethyl combine with the ethylenic linkage of maleic anhydride.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

# The Micro Estimation of Sulfur and Phosphorus in Organic Compounds

BY ADALBERT ELEK AND DOUGLAS W. HILL[1]

In a previous communication a micro-bomb was described for the quantitative micro determination of halogens in organic compounds.[2] The sample to be analyzed was oxidized in the bomb by means of sodium peroxide. From the success of the method in this instance it appeared probable that other estimations requiring a similar preliminary destruction of the organic material might be rapidly and successfully carried out in this apparatus. We therefore turned our attention to the estimation of organically bound sulfur and phosphorus.

Up to this time the majority of micro-estimations of sulfur in organic combination have been performed either by the combustion of the substance or by a micro modification of the Carius procedure. The use of the micro-bomb previously described[3] is much to be preferred to these methods in point of time, accuracy and ease of manipulation. The exact procedure for the determination is given in the experimental part.

The estimation of phosphorus has previously been accomplished by combustion of the substance or by heating it several times with a mixture of concentrated sulfuric and nitric acids with subsequent addition of perhydrol. A further method, which has been successfully employed in this Laboratory, was described by one of us[4] and involves the fusion of the sample under investigation with a mixture of potassium nitrate and po-

(1) Commonwealth Fund Fellow.

(2) Elek and Hill, THIS JOURNAL, **55**, 2550 (1933).

(3) Supplied by The Parr Instrument Co., Moline, Ill. (Since our previous communication illium alloy has been found to have certain advantages over platinum plating and the present bombs are constructed of this metal.)

(4) Elek, THIS JOURNAL, **50**, 1213 (1928).