TABLE I

MOLECULAR ROTATION DATA OF RING A AROMATIC STEROIDS[16]

Series	$[M]^{\text{Sat.}}_D$ (3β-Acetoxy-5α)	$[M]^{\text{IIIa}}_D$ (19-Nor-$\Delta^{1,3,5,6}$-tetraen-3-ol)	$[M]^{\text{IVa}}_D$ (19-Nor-$\Delta^{1,3,5}$-trien-3-ol)	$[M]^{\text{IX}}_D$ (19-Nor-1-methyl-3-acetoxy-$\Delta^{1,3,5,6}$-tetraene)	$[M]^{\text{X}}_D$ (19-Nor-1-methyl-3-acetoxy-$\Delta^{1,3,5}$-triene)	$[M]^{\text{IIIa}}_D - [M]^{\text{sat.}}_D$	$[M]^{\text{IVa}}_D - [M]^{\text{sat.}}_D$	$[M]^{\text{IX}}_D - [M]^{\text{sat.}}_D$	$[M]^{\text{X}}_D - [M]^{\text{sat.}}_D$
Androstan-17-one (dioxane)	+232[a]	−340[9a]	+437[9a]	−305[13a]	+714[13a]	−572	+205	−537	+482
Androstan-17β-ol acetate	− 9[a]	−633[9b]	+148[9b]	−548[13a]	+411[13a]	−624	+157	−539	+420
Methyl etianate	+135[b]	−215[c]	+339[c]	−294[c]	+721[c]	−350	+204	−429	+586
Δ^{16}-Pregnen-20-one	+150[d]	....	+349[6]	−350[6]	.....	...	+199	−500	...
Cholestane	+ 60[e]	−216[10]	+276[10]	−422[13c]	.....	−276	+216	−482	...
22a-Spirostane	−316[a]	−796[f]	− 75[f]	−810[f]	+212[f]	−480	+241	−498	+528

[a] Determined in these laboratories. [b] L. Ruzicka, E. Hardegger and C. Kauter, *Helv. Chim. Acta*, **27**, 1164 (1944). [c] A. Sandoval, G. Rosenkranz, C. Djerassi and F. Sondheimer, THIS JOURNAL, in press. [d] P. A. Plattner, L. Ruzicka, H. Heusser and E. Anliker, *Helv. Chim. Acta*, **30**, 385 (1947). [e] D. H. R. Barton, *J. Chem. Soc.*, 813 (1945). [f] This paper.

tone–hexane afforded 0.16 g. of the methoxy ketone VIb, m.p. 134–137°, λ_{max} 278 mμ (log ε 3.42), $\nu^{CHCl_3}_{max}$ 1700 cm.$^{-1}$. Identity with an authentic specimen[6] (m.p. 134–136°) was established through mixture m.p. determination and infrared comparison.

1-Methyl-19-nor-$\Delta^{1,3,5(10),6}$-22a-spirostatetraen-3-ol Acetate (IX).—A mixture of 3.0 g. of finely powdered $\Delta^{1,4,6}$-22a-spirostatrien-3-one (II)[8] suspended in 75 cc. of acetic anhydride containing 1.0 g. of *p*-toluenesulfonic acid was stirred at room temperature for 20 hours. As the reaction proceeded a homogeneous solution resulted, but after the 20-hour period a new precipitate had separated. This solid, which proved to be the desired rearrangement product, was collected and washed well with water; it weighed 0.69 g. and showed m.p. 164–169°. The filtrate was poured into water, the precipitated solid was taken up in ethyl acetate, and the solution was washed well with sodium bicarbonate and water, dried and evaporated. Trituration of the residue with methanol furnished another 0.22 g. (total yield 0.91 g., 28%) of the phenol acetate, m.p. 162–168°. The analytical sample was obtained through crystallization from chloroform–methanol and formed glistening plates, m.p. 170–172°, $[\alpha]_D$ −180°, λ_{max} 224 mμ (log ε 4.44) and 266 mμ (log ε 3.97), $\nu^{CHCl_3}_{max}$ 1744 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{29}H_{38}O_4$: C, 77.30; H, 8.50. Found: C, 77.62; H, 8.72.

When the above dienone phenol rearrangement was performed at steam-bath temperature, the same product could be isolated, but in considerably lower yield.

1-Methyl-19-nor-$\Delta^{1,3,5(10)}$-22a-spirostatrien-3-ol Acetate (X).—The tetraene acetate IX (0.50 g.) dissolved in 50 cc. of ethyl acetate was hydrogenated with 0.20 g. of a 5% palladium-on-charcoal catalyst overnight at atmospheric pressure and room temperature. Crystallization of the product from ethyl acetate–hexane furnished 0.39 g. of the triene acetate with m.p. 210–215°. The analytical specimen formed felted needles, m.p. 218–219°, $[\alpha]_D$ +47°, λ_{max} 270 mμ (log ε 2.57), $\nu^{CHCl_3}_{max}$ 1744 cm.$^{-1}$, no free hydroxyl band.

Anal. Calcd. for $C_{29}H_{40}O_4$: C, 76.95; H, 8.91. Found: C, 77.32; H, 9.08.

MEXICO CITY 17, D. F.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH SECTION, PICATINNY ARSENAL]

Contribution to the Chemistry of Benzfuroxan and Benzfurazan Derivatives

BY R. J. GAUGHRAN, J. P. PICARD AND J. V. R. KAUFMAN

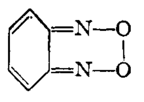
RECEIVED OCTOBER 2, 1953

Chemical and physical data are offered in support of the unsymmetrical quinonoid structure for benzfuroxan and its derivatives. The metallic salts obtained from 4,6-dinitrobenzfuroxan are discussed in view of structures previously postulated. Sufficient infrared data were obtained to establish the general absorption difference between benzfuroxan and benzfurazan. In addition, five new compounds were prepared: 5-methoxybenzfuroxan, 1,3-dinitro-4,6-diazidobenzene, 5-azido-6-nitrobenzfuroxan, nitrobenzdifuroxan and 5-methoxybenzfurazan.

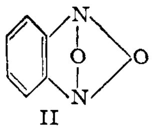
Introduction

The wide variety of applications suggested for benzfuroxan and its derivatives as dyes,[1] fungicides, parasiticides[2] and explosives[3] is mostly responsible for the numerous attempts found in the literature to elucidate its structure.

In 1907, Forster and Fierz[4] stated that benzfuroxan and its derivatives could not be considered true dinitroso compounds but should be regarded as dioxime peroxides, I. Green and his group[1] suggested the epoxide ring structure II and this structure subsequently received support from Forster, *et al.*,[5] who observed that no isomer due to the orientation of extra annular oxygen in structure III could be isolated. Hammick[6] (1931) studying the action of bromine upon benzfuroxan and benzfurazan derivatives obtained results which were interpreted as indicating that these compounds had quinonoid properties.



I



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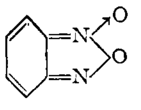

III

Of the three previously suggested structures, the peroxide and epoxide derivatives should be capable of forming symmetrical difuroxan compounds IV while such symmetrical derivatives would not be realized if the structure were *o*-quinonoid in nature.

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(1) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2457 (1912).

(2) Ter Horst, U. S. Patent 2,424,199(1947); *C. A.*, **41**, 7642 (1947).

(3) H. Rathsburg, British Patent 190,844 (1921); *C. A.*, **17**, 2960 (1923).

(4) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1943 (1907).

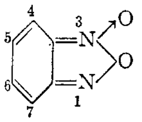
(5) M. O. Forster and M. F. Barker, *ibid.*, **103**, 1918 (1913).

(6) D. L. Hammick, W. A. M. Edwardes and E. R. Steiner, *ibid.*, 3308 (1931).

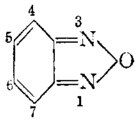
Table I

Physical Properties of Benzfuroxan and Benzfurazan Derivatives

Benzofuroxan



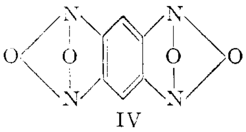
Benzfurazan



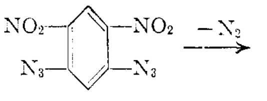
Substituent	Formula	M.p., °C.	Yield, %	Substituent	Formula	M.p., °C.	Yield, %
Benzfuroxan	$C_6H_4N_2O_2$	72	95	Benzfurazan	$C_6H_4N_2O$	53	40
4-Nitro	$C_6H_3N_3O_4$	143	60	4-Nitro	$C_6H_3N_3O_3$	93	40
4,6-Dinitro	$C_6H_2N_4O_6$	172	90				
5-Nitro	$C_6H_3N_3O_4$	72	93				
5-Methyl	$C_7H_6N_2O_2$	98	95	5-Methyl	$C_7H_6N_2O$	37	65
5-Methoxy	$C_7H_6N_2O_3$	118	95	5-Methoxy	$C_7H_6N_2O_2$	99	75
5,6-Dinitro	$C_6H_2N_4O_6$	172	40				
4,6-Dimethyl	$C_8H_8N_2O_2$	109	95	4,6-Dimethyl	$C_8H_8N_2O$	63	70
5-Azido-6-nitro	$C_6H_2N_6O_4$	89	60				
4-Nitro-5-methyl	$C_7H_5N_3O_4$	164	80				
4,6-Dinitro-5-methyl	$C_7H_4N_4O_6$	133	60				
4-Nitro-5-methoxy	$C_7H_5N_3O_5$	160	90				
5-Chloro	$C_6H_3N_2O_2Cl$	48	95	5-Chloro	$C_6H_3N_2OCl$	44	50

Thus if the symmetrical benzdifuroxan could not be prepared, this could be offered as evidence of the *o*-quinonoid structure suggested by Hammick.[6]

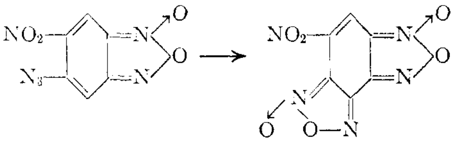
We have accordingly prepared 1,4-dinitro-2,5-diazidobenzene (V). When compound V was heated to 85°, nitrogen was slowly evolved. The resulting material VI was highly explosive. It was found to absorb at 4.75 μ, the characteristic band reported for the azido group. In addition it exhibited an absorption peak between 6.24 and 6.30 μ which was found during the course of this work to be characteristic of the benzfuroxan ring. These facts and its composition suggest the structure 4-azido-5-nitrobenzfuroxan (VI).



IV



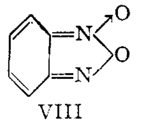
V



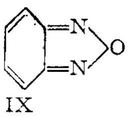
VI VII

Further heating of VI at higher temperature brought about explosive decomposition of the material. By further nitration of compound VI, an unstable substance resulted, which upon standing was converted into the more stable unsymmetrical nitrobenzdifuroxan VII. This is in agreement with Hammick's claim of *o*-quinonoid type of reactivity.

With this study additional information was gained by preparing various benzfuroxan VIII and benzfurazan IX derivatives (Table I) and studying their absorption spectra from 2 to 15 μ.



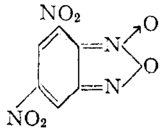
VIII



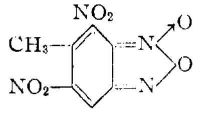
IX

One might expect the extra annular oxygen atom, which differentiates the benzfuroxan VIII from the benzfurazan IX to be equally shared between the two nitrogen atoms since no isomer could be isolated. However, such an unusual structure would have the tendency, in the double bond region, to show an increase in the number of absorption bands over that of a benzfurazan structure. When the infrared spectra of benzfuroxan and benzfurazan derivatives are compared between 6.0–6.5 μ (Fig. 1) the benzfuroxans have an additional band located between 6.24 and 6.30 μ. While complete spectra from 2 to 15 μ were obtained for each structure only pertinent segments of such spectra are shown for reason of space consideration.

Both benzfuroxan and benzfurazan derivatives can be nitrated and brominated. Benzfuroxan derivatives were transformed to the corresponding benzfurazans by reduction with hydroxylamine followed by steam distillation of the alkaline treated dioxime. The 4,6-dinitrobenzfuroxan (X) forms metal organic salts when treated with alkaline carbonates as claimed by Drost.[7] The anion present in these salts is probably produced by a loss of a proton from the quinonoid nucleus. The similarity between the infrared spectrum of 4,6-dinitrobenzfuroxan and its potassium salt (Fig. 2), suggests that salt formation was not due to the loss of a proton from any functional groups having a selective absorption, otherwise the two spectra would have been quite different. In addition, when 5-methyl-4,6-dinitrobenzfuroxan (XI) was treated with an inorganic carbonate, no salt was formed. It is suggested therefore that the loss of a proton from the quinonoid nucleus may be due to the inductive



X



XI

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[7] P. Drost, *Ann.*, **307**, 54 (1899).

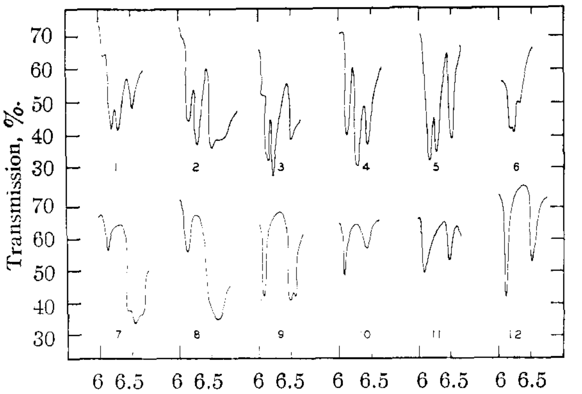

Fig. 1.—1, benzfuroxan; 2,4-nitrobenzfuroxan; 3, 5-methylbenzfuroxan; 4, 4,6-dimethylbenzfuroxan; 5, 5-methoxybenzfuroxan; 6, 5-chlorobenzfuroxan; 7, benzfurazan; 8, 4-nitrobenzfurazan; 9, 5-methylbenzfurazan; 10, 4,6-dimethylbenzfurazan; 11, 5-methoxybenzfurazan; 12, 5-chlorobenzfurazan.

effect of the two metal nitro groups in combination with the furoxan ring creating a low electron density spot at position 5.

In further attempts to elucidate its structure, the potassium derivative of 4,6-dinitrobenzfuroxan was treated with methyl chloride and methyl iodide successively in liquid ammonia. Alkylation was not detected although sodium halide was formed. Part of the starting material was recovered unchanged, and the rest obtained as the ammonium salt.

Experimental[8]

Potassium 4,6-Dinitrobenzfuroxan.—This salt was prepared according to the method of Drost[7] by neutralization of 4,6-dinitrobenzfuroxan with potassium bicarbonate followed by recrystallization from hot water. The product forms in small golden orange plates which explode at 210°.

Anal. Calcd. for $C_6NH_4O_6K$: C, 27.27; H, 0.38; N, 21.21; K, 14.77. Found: C, 27.53; H, 0.62; N, 21.25; K, 14.82.

Benzfuroxan, 5-Methylbenzfuroxan, 4,6-Dimethylbenzfuroxan, 5-Chlorobenzfuroxan and 5-Methoxybenzfuroxan.—These compounds were prepared by oxidation of the corresponding *o*-nitroamino compounds by sodium hypochlorite, following the procedure reported by Green and Rowe.[1] For example, in the preparation of 5-methoxybenzfuroxan, 10 g. of 3-nitro-4-aminoanisole was suspended in 150 cc. of saturated alcoholic sodium hydroxide solution. To this was added with cooling commercial aqueous sodium hypochlorite till the red color disappeared; the fluffy yellow precipitate formed was filtered, washed with cold water and recrystallized from ethanol.

Anal. Calcd. for $C_7H_6N_2O_3$: C, 50.60; H, 3.22; N, 16.86. Found: C, 50.64; H, 3.22; N, 16.79.

4-Nitrobenzfuroxan, 4,6-Dinitrobenzfuroxan, 4-Nitro-5-methylbenzfuroxan and 4,6-Dinitro-5-methylbenzfuroxan.—These compounds were prepared in good yields according to the method of Green, *et al.*,[1] and Drost.[7] The procedure in general consists of dissolving the benzfuroxan derivatives in six parts of 96% sulfuric acid and nitrating at 5–20° with a 4 to 1 sulfuric–nitric acid mixture. An equimolecular quantity of 100% nitric acid was used.

5-Nitrobenzfuroxan.—The method given by Drost[7] for the preparation of this compound was lengthy and tedious. The following method is more rapid and convenient. Five grams of 2,4-dinitroaniline was dissolved by warming in a mixture of 40 ml. of acetic acid and 20 ml. of sulfuric acid. To this ice was added to maintain the temperature between 0 and 5° during the addition of sufficient sodium nitrite to obtain a clear solution. The excess nitrous acid was removed by adding urea. The addition of a slight excess of sodium azide with vigorous stirring gave a white fluffy precipitate. The mass was separated by filtration and while still wet was heated at 75° on a steam-bath until the evolution of nitrogen ceased. The resulting material was recrystallized from hot ethanol; upon cooling 4.5 g. (93% of theory) of yellow plates, m.p. 72°, was obtained. This is in agreement with the melting point reported by Drost[7] for 5-nitrobenzfuroxan.

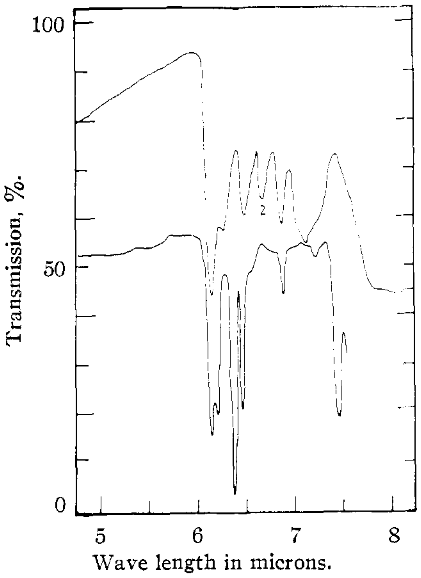

Fig. 2.—1, 4,6-dinitrobenzfuroxan; 2, potassium salt of 4,6-dinitrobenzfuroxan.

1,3-Dinitro-4,6-diazidobenzene (V).—Six and one-half grams of sodium azide was dissolved in a mixture of 20 ml. of water, 20 ml. of alcohol and 10 ml. of acetone. To this was added slowly, with rapid stirring at room temperature, a solution of 10 g. of 1,3-dinitro-4,6-dichlorobenzene in 34 ml. of acetone. Toward the end of the addition glistening rectangular yellow platelets precipitated. After recrystallization from ethanol the material had a m.p. of 78°. This compound when heated above its melting point exploded with violence. The analysis corresponds to 1,3-dinitro-4,6-diazidobenzene.

Anal. Calcd. for $C_6H_2N_8O_4$: C, 28.80; H, 0.80; N, 44.80. Found: C, 28.76; H, 1.37; N, 43.55.

5-Azido-6-nitrobenzfuroxan (VI).—This compound resulted from the thermal decomposition of 1,3-dinitro-4,6-diazidobenzene. One gram of the latter was placed in a test-tube equipped with a bubbler to indicate the evolution of gas. The tube was heated slowly to 80–85° in a water-bath and maintained at that temperature until the evolution of nitrogen ceased. The residue was then cooled and recrystallized twice from alcohol. The product, glistening dark yellow needles, melted at 89° with decomposition. It explodes violently when heated rapidly above its melting point.

Anal. Calcd. for $C_6H_2N_6O_4$: C, 32.43; H, 0.90; N, 37.83. Found: C, 32.48; H, 1.17; N, 37.69.

Nitrobenzdifuroxan (VII).—To a mixture of 0.5 g. of phosphorus pentoxide and 40 ml. of anhydrous nitric acid was slowly added with stirring, 5 g. of 4-nitro-5-azidobenzfuroxan. When the addition was complete the mixture was stirred for an additional five minutes to assure complete solution. The solution was then drowned in ice-water. An orange-yellow flocculent precipitate resulted which upon filtering yielded a sticky mass. The isolated material decomposed almost immediately with evolution of nitrogen. A low yield of material was obtained (approx. 10%) which after two recrystallizations from ethanol gave yellow plates melting at 156°, VII.

Anal. Calcd. for $C_6H_2N_5O_6$: C, 30.12; H, 0.41; N, 29.29. Found: C, 30.07; H, 1.14; N, 29.99.

Attempts to Prepare Symmetrical Benzdifuroxan.—If the structure of benzfuroxan derivatives were anything but or-

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[8] All melting points are corrected.

thoquinonoid, it would be possible to prepare a symmetrical benzdifuroxan upon pyrolysis of 1,4-dinitro-2,5-diazidobenzene (V) or 4-nitro-5-azidobenzfuroxan (VI). Both of these compounds upon prolonged heating above 90° decomposed without giving any recrystallizable material. Heating below this temperature, V gave 4-nitro-5-azidobenzfuroxan (VI) while further heating resulted in total decomposition.

Benzfurazan, 5-Methylbenzfurazan, 5-Chlorobenzfurazan, 4,6-Dimethylbenzfurazan, 4-Nitrobenzfurazan, and 5-Methoxybenzfurazan.—These compounds were all prepared according to the method described by Zincke and Schwarz[9] by reduction of the parent furoxan with hydroxylamine followed by steam distillation of the alkaline solution, except for the 4-nitrobenzfurazan which was obtained by nitration of benzfurazan with mixed acid as described above. For example, in the preparation of 5-methoxybenzfurazan, 5 g. of methoxybenzfuroxan was dissolved in 75 cc. of alcohol and 7.5 g. of hydroxylamine hydrochloride in a minimum amount of water was added. An aqueous 25% sodium hydroxide solution was then added till gas evolution ceased. The alcohol was evaporated and the residue made alkaline and steam distilled. The 5-methoxybenzfurazan was obtained in 75% yield.

Anal. Calcd. for $C_7H_6N_2O_2$: C, 56.00; H, 4.00; N, 18.66. Found: C, 56.21; H, 4.22; N, 18.62.

Dover, New Jersey

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(9) T. Zincke and P. Schwarz, *Ann.*, **307**, 40 (1899).

[Contribution from the Department of Chemistry, Washington University]

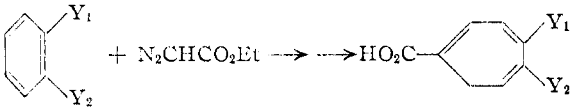
Reactions of Ethyl Diazoacetate with Aromatic Compounds Containing Hetero Atoms Attached to the Benzyl Carbon

By C. David Gutsche and Manny Hillman[1]

Received October 17, 1953

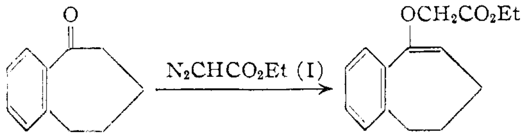
The reactions of ethyl diazoacetate with various aromatic compounds containing hetero atoms attached to the benzyl carbon have been studied, and in all cases the benzyl position was found to be involved in preference to the aromatic nucleus. Thus, benzosuberone yielded ethyl 6,7-dihydro-5H-cycloheptabenzene-9-oxyacetate (II), benzal chloride yielded ethyl α-chlorocinnamate (III), 2-phenyl-1,3-dioxolane yielded both stereoisomeric forms of ethyl 3-phenyl-2-*p*-dioxanecarboxylate (IV), and 2-phenyl-2-methyl-1,3-dioxolane yielded ethyl 3-methyl-3-phenyl-2-*p*-dioxanecarboxylate (XI). The last two reactions are unusual in that a ring enlargement of a 1,3-dioxolane ring to a *p*-dioxane ring is involved. In addition to the dioxane XI, 2-phenyl-2-methyl-1,3-dioxolane also yielded a very small amount of acetylcycloheptatrienecarboxylic acid (XIII), the product resulting from attack of the ethyl diazoacetate on the phenyl nucleus.

The present investigation had its inception in our search for a method of preparation of cycloheptatrienes carrying actual or potential aldehydo or acyl groups. It was hoped that the well-known ring enlargement of benzene by means of ethyl diazoacetate might be applicable and that conversions of the type shown below might be effected



In only one of the four cases studied, however, was any of the desired product isolated, and it was produced in such small amount as to be impractical from the synthetic standpoint. In all instances the main reaction involved the nuclear substituent Y rather than the benzene nucleus itself.

Ethyl Diazoacetate and Benzosuberone (Y_1,Y_2 = $-CO(CH_2)_4-$).—Benzosuberone reacted smoothly with ethyl diazoacetate (I) at 120–160° to give a product in 50.5% yield whose chemical behavior is best rationalized in terms of the enol ether II. This material reacted with semicarbazide and with 2,4-dinitrophenylhydrazine under acidic conditions to form the semicarbazone and 2,4-dinitrophenylhydrazone of benzosuberone. Treatment with *p*-nitrobenzaldehyde resulted in no reaction unless preceded by an acid hydrolysis, in which case the product was the *p*-nitrobenzylidene derivative of benzosuberone. This acid lability is characteristic of enol ethers. The formation of an amide possessing the correct analysis, the permanganate oxidation to γ-(2-carboxyphenyl)-butyric acid and the ultraviolet spectrum which showed a strong absorption at 250 mμ[2] further substantiated the postulated structure.



II

Reactions have been reported between ethyl diazoacetate and various carbonyl compounds including benzaldehyde,[3,4] halogenated aliphatic aldehydes,[5] *n*-heptaldehyde,[4] alloxans,[6] diphenylketene,[7] acetone and cyclohexanone.[8] Of these, acetone and cyclohexanone are reported to yield enol ethers, in correspondence with the results obtained with benzosuberone.

Ethyl Diazoacetate and Benzal Chloride (Y_1 = $CHCl_2$, Y_2 = H).—Benzal chloride and ethyl diazoacetate reacted at 160–175° to yield 24% of a product which proved to be ethyl α-chlorocinnamate (III). The structure proof is based on the conversion to the known amide, the formation of 3-phenylpyrazolone-5 upon treatment with hydrazine, saponification to α-chlorocinnamic acid, and

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(1) du Pont predoctoral fellow 1952–1953.

(2) D. S. Horn and W. S. Rapson, *J. Chem. Soc.*, 2421 (1949), report the ultraviolet spectrum of 6,7-dihydro-5H-cycloheptabenzene as ϵ_{max} 254 mμ (15,600).

(3) E. Buchner and T. Curtius, *Ber.*, **18**, 2371 (1885); T. Curtius, *J. prakt. Chem.*, **38**, 394 (1888).

(4) W. Dieckmann, *Ber.*, **43**, 1024 (1910).

(5) F. Schlotterbeck, *ibid.*, **40**, 3000 (1907); **42**, 2565 (1909).

(6) H. Biltz and E. Kramer, *Ann.*, **436**, 154 (1924).

(7) H. Staudinger and T. Reber, *Helv. Chim. Acta*, **4**, 3 (1921).

(8) M. S. Kharasch, T. Rudy, W. Nudenberg and G. Buchi, *J. Org. Chem.*, **18**, 1030 (1953). We are indebted to one of the referees for calling our attention to this paper which appeared after our work had been completed and which we had overlooked.