alkaline solution acidified, then crystallized from nitromethane, m.p. 145°, yield 17 g. (47%).

2,3-Dimethylbenzoyl chloride[9] was prepared from 16 g. of the acid, which was refluxed for 4 hours with 15 g. of thionyl chloride; b.p. 98–100° (3 mm.), yield 13 g. (68%).

(2,3-Dimethylbenzoyl)-cyclohexene (VIII).—Following the method of Christ and Fuson,[10] 10.5 g. of aluminum chloride was added (in 5 portions), at 0° and during 1 hour, to a well-agitated mixture of 13 g. of 2,3-dimethylbenzoyl chloride, 6.5 g. of cyclohexene and 50 ml. of carbon disulfide. The reaction mixture was stirred at 0° for another 6 hours, decomposed with ice and hydrochloric acid and concentrated *in vacuo*. The residue was refluxed for 3 hours with a solution of 4.4 g. of potassium hydroxide in 20 ml. of ethanol and the alcohol removed *in vacuo*. The residue was then diluted with water, extracted with ether and distilled; b.p. 133–135° (0.4 mm.), $n^{26}\text{D}$ 1.5598, yield 9 g. (55%), $\nu_{\max}^{\text{liq}}$ 1631 cm.$^{-1}$; $\lambda_{\max}^{\text{EtOH}}$ 255 mμ (4.20), inflection at 327 mμ (2.42).

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.6. Found: C, 83.2; H, 8.6.

The 2,4-dinitrophenylhydrazone crystallized from isopropyl alcohol as orange needles, m.p. 155°; $\lambda_{\max}^{\text{CHCl}_3}$ 258 mμ (4.45), 295 mμ (4.26), 394 mμ (4.48).

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.9; H, 5.6. Found: C, 63.6; H, 5.5.

1,2-Dimethyl-5,5a,6,7,8,8a-hexahydrofluorenone (IX).—A mixture of 7 g. of VIII, 17 g. of phosphoric acid (90%) and 55 g. of formic acid (98%) was kept at room temperature for 12 hours and at 85–90° for 6 hours, diluted with water and extracted with ether. The product IX was isolated by distillation *in vacuo*; b.p. 122–123° (0.15 mm.), $n^{26}\text{D}$ 1.5633, yield 4.2 g. (60%); $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (4.11), 291 mμ (3.40); $\nu_{\max}^{\text{KBr}}$ 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.4. Found: C, 83.6; H, 8.0.

The 2,4-dinitrophenylhydrazone crystallized from butanol as red needles, m.p. 213°, $\lambda_{\max}^{\text{CHCl}_3}$ 398 mμ (4.52).

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.9; H, 5.6. Found: C, 64.4; H, 6.3.

1,2-Dimethylfluorenone.—A mixture of 4 g. of IX and 2 g. of sulfur was heated at 250° for 5 hours and the product extracted with benzene. It was purified by chromatography on alumina, but proved to be an oil; b.p. 127–130° (0.7 mm.), yield 3 g. (79%); $\lambda_{\max}^{\text{EtOH}}$ 264 mμ (4.62), 397 mμ (4.50); $\nu_{\max}^{\text{liq}}$ 1715 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.7; H, 5.9.

The 2,4-dinitrophenylhydrazone was obtained from nitromethane as orange-red crystals, m.p. 257°.

Anal. Calcd. for $C_{21}H_{16}N_4O_4$: C, 64.9; H, 4.1. Found: C, 64.3; H, 4.2.

1,2-Dimethylfluorene (V).—The hydrocarbon, obtained from 2.5 g. of 1,2-dimethylfluorenone, 1.5 g. of powdered potassium hydroxide, 1.5 ml. of hydrazine hydrate (100%) and 12 ml. of diethylene glycol, was an oil, b.p. 125–128° (2 mm.), yield 2 g. (87%).

Anal. Calcd. for $C_{15}H_{14}$: C, 92.8; H, 7.2. Found: C, 93.1; H, 7.3.

JERUSALEM, ISRAEL

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[10] R. E. Christ and R. C. Fuson, THIS JOURNAL, **75**, 3306 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, AIN SHAMS UNIVERSITY]

The Stobbe Condensation of Diethyl Phenylsuccinate with Cycloheptanone

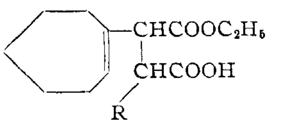
BY A. M. ISLAM AND M. T. ZEMAITY

RECEIVED FEBRUARY 10, 1957

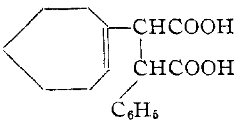
Condensation of diethyl phenylsuccinate and cycloheptanone in the presence of potassium *t*-butoxide gives β-carbethoxy-β-(cyclohepten-1-yl)-α-phenylpropionic acid (Ia). This is cyclized to 9-phenylbicyclo[5:3:0]dec-1(7)-en-8-one (IV), together with α-cycloheptenyl-β-phenylsuccinic acid (II). Saponification of Ia with alkali gives cycloheptylidenephenylsuccinic acid (IIIa).

The aim of the present investigation was to study the Stobbe condensation of diethyl phenylsuccinate with cycloheptanone in the hope of obtaining the bicyclic ketone IV.

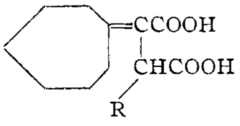
Condensation of diethyl phenylsuccinate with cycloheptanone in the presence of sodium ethoxide gives only ethyl α-phenylhydrogensuccinate. In the presence of potassium *t*-butoxide, however, the product is almost entirely the cycloheptenyl half-ester Ia.



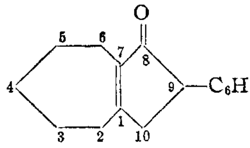
Ia, R = C_6H_5
Ib, R = H



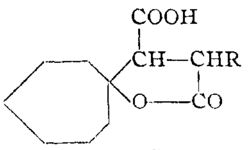
II



IIIa, R = C_6H_5
IIIb, R = H



IV



Va, R = C_6H_5
Vb, R = H

The ultraviolet absorption spectrum of Ia is very similar to that of phenylsuccinic acid and thus the double bond is pictured in the endocyclic position. This is in agreement with Stobbe's generalization[1] that compounds with methylene groups flanking the carbonyl group usually assume the pyrotartaric acid structure.

Treatment of this half-ester Ia with a hot mixture of acetic acid and hydrochloric acid furnishes a product which gives carbon and hydrogen figures corresponding to the three isomeric compounds II, IIIa and Va.

In contrast to Cook, *et al.*,[2] who isolated the cycloheptylidene compound IIIb together with the paraconic acid Vb on treating the half-ester Ib with acetic acid–hydrochloric acid mixture, our product is almost entirely the cycloheptenyl acid II. Its

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[1] H. Stobbe, *Ann.*, **321**, 83 (1902).

[2] J. W. Cook, R. Philip and A. R. Somerville, *J. Chem. Soc.*, 164 (1948).

neutral equivalent shows that it is a dibasic acid, and on oxidation with alkaline permanganate, no cycloheptanone was isolated. The endocyclic position of the double bond in II is plausible as a prototropic rearrangement under acid conditions is unlikely.

When this acid, however, is treated with alcoholic sodium methoxide it is isomerized to IIIa.

Saponification of the half-ester Ia with sodium or barium hydroxide gives a dibasic acid which is identical with the cycloheptylidene acid IIIa. In contrast to the cycloheptenyl acid II, this acid is readily converted to the anhydride when treated with acetyl chloride at room temperature, a characteristic feature of itaconic acids.[3,4]

Oxidation of IIIa with alkaline permanganate gives cycloheptanone, thus demonstrating conclusively the exocyclic position of the double bond. However, the ultraviolet absorption spectrum of IIIa shows no characteristic absorption near 220 mμ as reported by Plattner and Buchi[5] for the cycloheptylidene acid IIIb. The non-appearance of the characteristic absorption of the α,β-unsaturated acid grouping in IIIa may be attributed to the fact that the carbonyl group is practically inhibited from conjugation with the double bond by the bulky $C_6H_5\underset{|}{C}HCOOH$ group.

Cyclization of the half-ester Ia with acetic anhydride–acetic acid mixture containing catalytic amounts of zinc chloride gives a product which is separated into an acidic and a neutral fraction. The acidic fraction is mainly the dibasic acid II as proved by melting point and mixed melting point determinations. The neutral oily part of the product gives a 2,4-dinitrophenylhydrazone and is characterized as the bicyclic ketone IV.

Experimental[6]

β-Carbethoxy-β-(cyclohepten-1-yl)-α-phenylpropionic Acid (Ia).—To a cold solution of potassium *t*-butoxide (from 4.3 g. of potassium metal and 100 ml. of *t*-butyl alcohol) was added a mixture of 11.2 g. of cycloheptanone and 37.5 g. of diethyl phenylsuccinate under an atmosphere of nitrogen and the reaction mixture was heated under reflux for 45 minutes. The cold reaction mixture was acidified with a mixture of 20 ml. of concentrated hydrochloric acid and 20 g. of ice. Most of the *t*-butyl alcohol was removed under reduced pressure and the residue was extracted with ether. The ether layer was extracted thoroughly with saturated sodium bicarbonate solution. Acidification of the aqueous extracts with dilute hydrochloric acid liberated the half-ester which was taken up in ether. Evaporation of the ether gave 13.6 g. (43%) of crude β-carbethoxy-β-(cyclohepten-1-yl)-α-phenylpropionic acid (Ia), m.p. 146–148°, which crystallized from dilute ethyl alcohol in colorless needles, m.p. 148–150° (12.5 g.).

Anal. Calcd. for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.60; H, 7.81.

Ultraviolet absorption spectrum in ethyl alcohol exhibited a maximum at 260 (ε 587) and a minimum at 250 mμ (ε 323). Phenylsuccinic acid in ethyl alcohol exhibited a maximum at 260 (ε 115) and a minimum at 250 mμ (ε 46).

Cycloheptylidenephenylsuccinic Acid (IIIa).—A mixture of 1 g. of Ia and 2 g. of barium hydroxide octahydrate in 16 ml. of water was heated on the water-bath for 7 hours. The cold reaction mixture was acidified carefully with dilute hydrochloric acid and extracted with ether. Evaporation of the ether gave 0.8 g. (88%) of cycloheptylidenephenylsuccinic acid (IIIa), m.p. 169–172°, which crystallized from dilute ethyl alcohol in colorless needles, m.p. 172–174° (0.72 g.). Ultraviolet absorption spectrum in ethyl alcohol exhibited a maximum at 260 (ε 377) and a minimum at 245 mμ (ε 136).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99; neut. equiv., 144. Found: C, 70.57; H, 7.10; neut. equiv., 139.

Cycloheptylidenephenylsuccinic acid (IIIa) also was obtained (80%) on saponification of Ia with a 10% sodium hydroxide solution under nitrogen atmosphere (m.p. and mixed m.p.).

Cycloheptylidenephenylsuccinic Anhydride.—The crude cycloheptylidenephenylsuccinic acid (IIIa) (0.6 g.) was treated with 24 ml. of freshly distilled acetyl chloride, and the mixture was left to stand at room temperature for one and a half hours. The acetyl chloride was removed under reduced pressure and the residue taken up in ether. The ether solution was extracted several times with sodium bicarbonate solution, washed with water and dried. Evaporation of the ether gave 0.5 g. (90%) of cycloheptylidenephenylsuccinic anhydride which crystallized from ether-petroleum ether (b.p. 40–60°) in colorless needles, m.p. 110–112°. Ultraviolet absorption spectrum in ethyl alcohol exhibited a maximum at 262.5 (ε 72) and a minimum at 255 mμ (ε 36).

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.44; H, 6.68.

The alkaline aqueous extracts from the above experiment was acidified with dilute hydrochloric acid and extracted with ether. No product was isolated on evaporation of the ether.

When cycloheptylidenephenylsuccinic anhydride was hydrolyzed by heating on the water-bath for 8 hours with saturated sodium bicarbonate solution, cycloheptylidenephenylsuccinic acid (IIIa) was obtained (94%) (m.p. and mixed m.p.).

Permanganate Oxidation of IIIa.—A warm solution of 1 g. of IIIa in a saturated solution of sodium carbonate was treated, portionwise, with an aqueous dilute potassium permanganate solution until the color of the permanganate persisted. After being left to stand for two hours, the reaction mixture was extracted with ether, and the ether washed and dried. The ether then was evaporated and the residue was treated with an alcoholic solution of 2,4-dinitrophenylhydrazine sulfate. The resultant product proved to be cycloheptanone 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with an authentic sample of the derivative).

α-Cycloheptenyl-β-phenylsuccinic Acid (II).—A mixture of 1 g. of Ia, 10 ml. of concentrated hydrochloric acid and 15 ml. of glacial acetic acid was heated under reflux for 5 hours. The reaction mixture was concentrated under reduced pressure, diluted with water and extracted with ether. Evaporation of the ether gave 0.9 g. (98%) of α-cycloheptenyl-β-phenylsuccinic acid (II), m.p. 158–160°, which crystallized from dilute ethyl alcohol in colorless needles, m.p. 162° (0.82 g.).

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99; neut. equiv., 144. Found: C, 70.97; H, 6.76; neut. equiv., 142.

Oxidation of II with alkaline potassium permanganate afforded no cycloheptanone.

Cyclization of (Ia).—A mixture of 2.5 g. of Ia, 25 ml. of acetic anhydride and 25 ml. of a solution of fused zinc chloride in acetic acid (20 mg./ml.) was heated under reflux for 4 hours under nitrogen atmosphere. After being cooled, the reaction mixture was carefully diluted with 50 ml. of water followed by the addition of 20 ml. of concentrated hydrochloric acid. Heating under reflux was continued for another 45 minutes under nitrogen atmosphere. The cold reaction mixture was diluted with water and extracted several times with ether. The combined ether extracts were washed with dilute sodium hydroxide solution. Evaporation of the ether and distillation gave 1.1 g. (61%) of 9-phenylbicyclo-[5:3:0]dec-1(7)-en-8-one (IV) as a colorless oil, b.p. 73° (0.2 mm.).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.95; H, 7.96. Found: C, 84.82; H, 7.74.

The 2,4-dinitrophenylhydrazone crystallized from ethyl alcohol–ethyl acetate mixture in dark red plates, m.p. 156–158°.

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(3) H. Stobbe, *Ann.*, **308**, 67 (1899).

(4) W. S. Johnson and A. Goldman, THIS JOURNAL, **66**, 1030 (1944).

(5) P. A. Plattner and G. Buchi, *Helv. Chim. Acta*, **29**, 1608 (1946).

(6) Melting points are not corrected.

Ultraviolet absorption spectrum of the 2,4-dinitrophenylhydrazone in ethyl alcohol exhibited a maximum at 395 mμ (ε 41,870). Braude and Forbes[7] record for the 2,4-dinitrophenylhydrazone of 10-methylbicyclo[5:3:0]dec-1(7)-en-8-one λ_{max} 394 mμ (ε 26,000) in chloroform.

Anal. Calcd. for $C_{22}H_{22}N_4O_4$: C, 65.01; H, 5.46; N, 13.79. Found: C, 65.36; H, 5.65; N, 13.55.

The aqueous alkaline solution from the above experiment was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the ether gave 0.6 g. (28%) of an acid which crystallized from dilute ethyl alcohol in colorless needles, m.p. 162°, undepressed by an authentic sample of α-cycloheptenyl-β-phenylsuccinic acid (II) obtained above.

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(7) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 2208 (1953).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

5,7-Dinitro-3-coumaranone and the Mechanism of the Bimolecular Nucleophilic Displacement Reaction in Phenacyl Compounds[1a]

BY PAUL D. BARTLETT AND EDWARD N. TRACHTENBERG[1b]

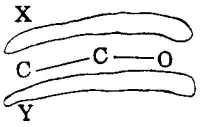
RECEIVED MAY 3, 1958

5,7-Dinitro-3-coumaranone (I) has been synthesized as a model phenacyl pseudo-halide free of steric hindrance to displacement of the dinitrophenoxide group but requiring any attacking reagent to enter the molecule in the plane of the 5-membered ring and of the carbonyl group. In reaction with potassium iodide in acetone, I shows $\Delta H^{\ddagger} = 31.3 \pm 1.9$ kcal., $\Delta S^{\ddagger} = 25.4 \pm 6.0$ cal./degree. For comparison ω-(4-aceto-2,6-dinitro)-phenoxyacetophenone (II) has $\Delta H^{\ddagger} = 10.2 \pm 1.2$ kcal. and $\Delta S^{\ddagger} = -30.0 \pm 4.4$ cal./degree. These results indicate a stereochemical requirement for the special reactivity of phenacyl halides; mechanisms in which such a requirement is implicit are discussed.

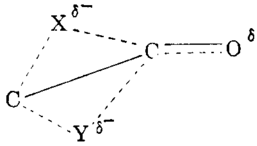
It has long been known that α-haloketones show remarkably enhanced reactivity in bimolecular nucleophilic displacement (SN2) reactions. For this behavior, which is also displayed to a lesser degree in α-halo nitriles, amides, esters and carboxylate anions, explanations of several different kinds have been offered. The suggestion has been made[2] that inductive electron withdrawal by the carbonyl group activates the adjacent saturated carbon toward nucleophilic displacement. Pearson and co-workers[3] proposed that the proximity of the positively charged carbon atom of the carbonyl group electrostatically facilitates approach of the displacing reagent along its normal path to the adjacent carbon atom. At the other extreme, covalent bond formation of the reagent with the carbonyl carbon atom has been viewed as a possibility,[4] to be followed by intramolecular rearrangement and displacement. In a variant of this mechanism of covalent participation, the possibility of epoxide formation in a follow-up step was considered; strong arguments have been brought against both of these schemes.[3] Finally, two mechanisms based upon orbital overlap without complete covalent bonding to carbonyl carbon have been proposed by Dewar[5] and by Winstein[6]; in both cases the approach of the reagent is regarded as facilitated, not by electrostatic or inductive effects, but by partial overlap, respectively, with the π-molecular orbital of the C–C–O system or with the p-orbital of the carbonyl carbon.

There is evidence to indicate that inductive electron withdrawal from a carbon atom does not in general increase, but may rather decrease, the ease of a displacement reaction at that carbon atom. This can be seen in alkyl halides substituted at the β-position by halogen[7] or alkoxyl.[8] A less clear case is the unreactivity of α-halosulfones,[9,10] or of chloroacetylmesitylene,[11] where steric factors cannot be ruled out.

The mechanisms of Dewar and of Winstein have a stereochemical implication which has suggested the experiments of this paper. In both, the atoms C—C=O of the phenacyl side chain determine a plane, and the entering and departing groups in the displacement reaction must occupy positions above and below that plane in order to find the orbitals of the two adjacent carbon atoms with which they are to interact.



A (delocalized orbital)



B (localized orbitals)

Any structural feature of a phenacyl halide or pseudo-halide which would prevent the YCCX plane from being perpendicular to the CCO plane in a transition state for displacement should sharply raise the energy of that transition state if A or B is a correct picture of the reaction. It is not possible to put such constraints on a halogen atom; however, the fact that a 2,4- or 2,6-dinitrophenoxy group can be displaced as an anion makes possible the construction of I, whose reactivity in comparison with II should provide the desired test.

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(1) (a) Presented at the 14th International Congress of Pure and Applied Chemistry, Zurich, 1955. (b) Standard Oil (Indiana) Fellow, 1951–1952.

(2) E. D. Hughes, *Quart. Revs.*, **5**, 245 (1951).

(3) R. G. Pearson, S. H. Langer, F. V. Williams and W. J. McGuire, THIS JOURNAL, **74**, 5130 (1952).

(4) J. W. Baker, *Trans. Faraday Soc.*, **37**, 632 (1941).

(5) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p. 73.

(6) Suggested by S. Winstein at the International Colloquium on Molecular Rearrangements and Walden Inversion at Montpellier, France, 1950; see S. Winstein, E. Grunwald and H. W. Jones, THIS JOURNAL, **73**, 2700 (1951), footnote 16.

(7) J. Hine and W. H. Brader, Jr., *ibid.*, **75**, 3964 (1953).

(8) F. B. Tutwiler and R. L. McKee, *ibid.*, **76**, 6342 (1954).

(9) T. B. Johnson and I. B. Douglass, *ibid.*, **63**, 1571 (1941).

(10) F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5184 (1951).

(11) S. H. Babcock, F. I. Nakamura and R. C. Fuson, *ibid.*, **54**, 4407 (1932).